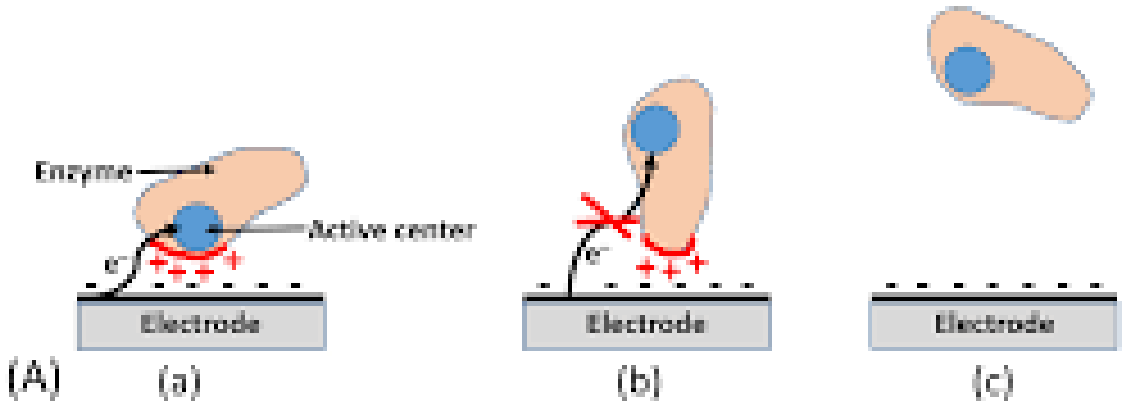
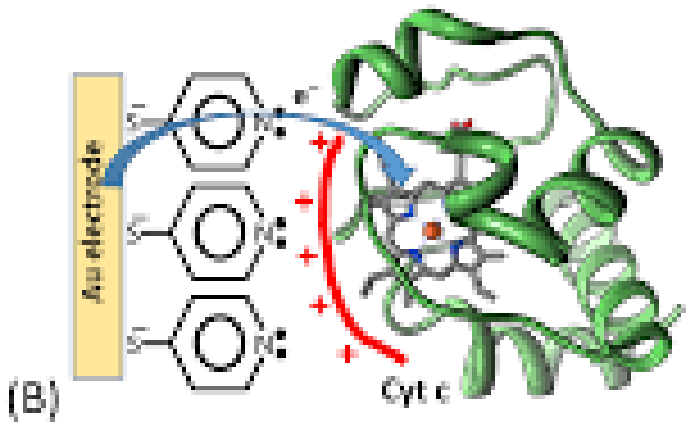
Square-wave voltammetry of Lipophilic Redox Enzymes Featuring Electrode Reaction Associated with Two Reversible Chemical Steps

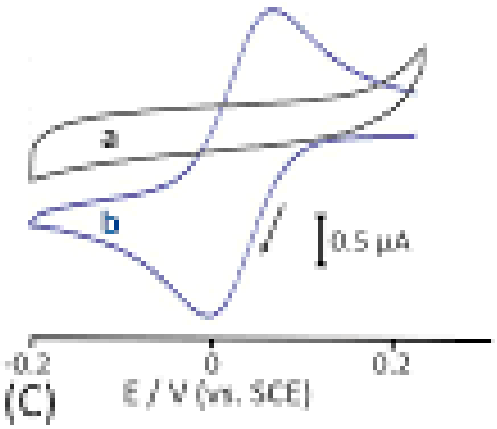
Pavlinka Kokoskarova, Sonja Risafova, Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University Stip
MACEDONIA

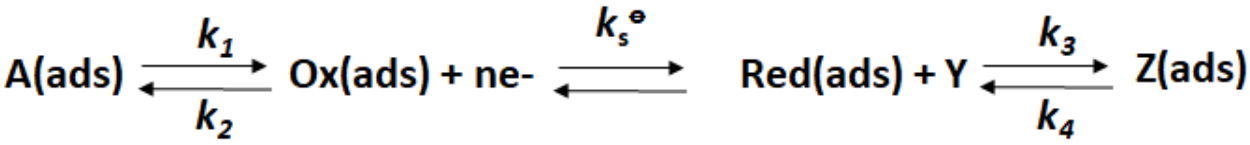
$$A(ads) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ox(ads) + ne^- \overset{k_s^e}{\rightleftharpoons} Red(ads) + Y \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Z(ads)$$







The model we consider is a surface electrode mechanism Whose electron transfer step is associated with preceding and follow up reversible chemical reactions



$t = 0$; $\Gamma(\mathrm{A}) = \Gamma^*(\mathrm{A})$; $\Gamma(\mathrm{Ox}) = K_{eq}\,\Gamma^*(\mathrm{A})$; $\Gamma(\mathrm{Red}) = 0$ (a)

$t > 0$; $\Gamma(\mathrm{A}) + \Gamma(\mathrm{Ox}) + \Gamma(\mathrm{Red}) + \Gamma(\mathrm{Z}) = \Gamma^*(\mathrm{A})$; (b)

$t > 0$; $K_{eq,\,preceding} = k_1/k_2$; $K_{eq,\,follow\text{-}up} = k_3/k_4$ (c)

For $t > 0$, the following differential equations (d-f) link the surface concentrations with the current and the kinetics and thermodynamics of preceding and follow-up chemical steps:

$$(\mathrm{d}\Gamma(\mathrm{A})/\mathrm{d}t) = k_1\Gamma(\mathrm{Ox}) - k_2\Gamma(\mathrm{A}) \quad \text{(d)}$$

$$\mathrm{d}\Gamma(\mathrm{Ox})/\mathrm{d}t = -I/(nFS) - k_2\Gamma(\mathrm{Ox}) + k_1\Gamma(\mathrm{A}) \quad \text{(e)}$$

$$\mathrm{d}\Gamma(\mathrm{Red})/\mathrm{d}t = I/(nFS) + k_3\Gamma(\mathrm{Red}) - k_4\Gamma(\mathrm{Z}) \quad \text{(f)}$$

The electric current, the applied electrical potential difference, the surface concentrations of the electrochemically active species, and the other parameters relevant to electron transfer step are assumed to be interrelated via the Butler-Volmer equation, having the following form:

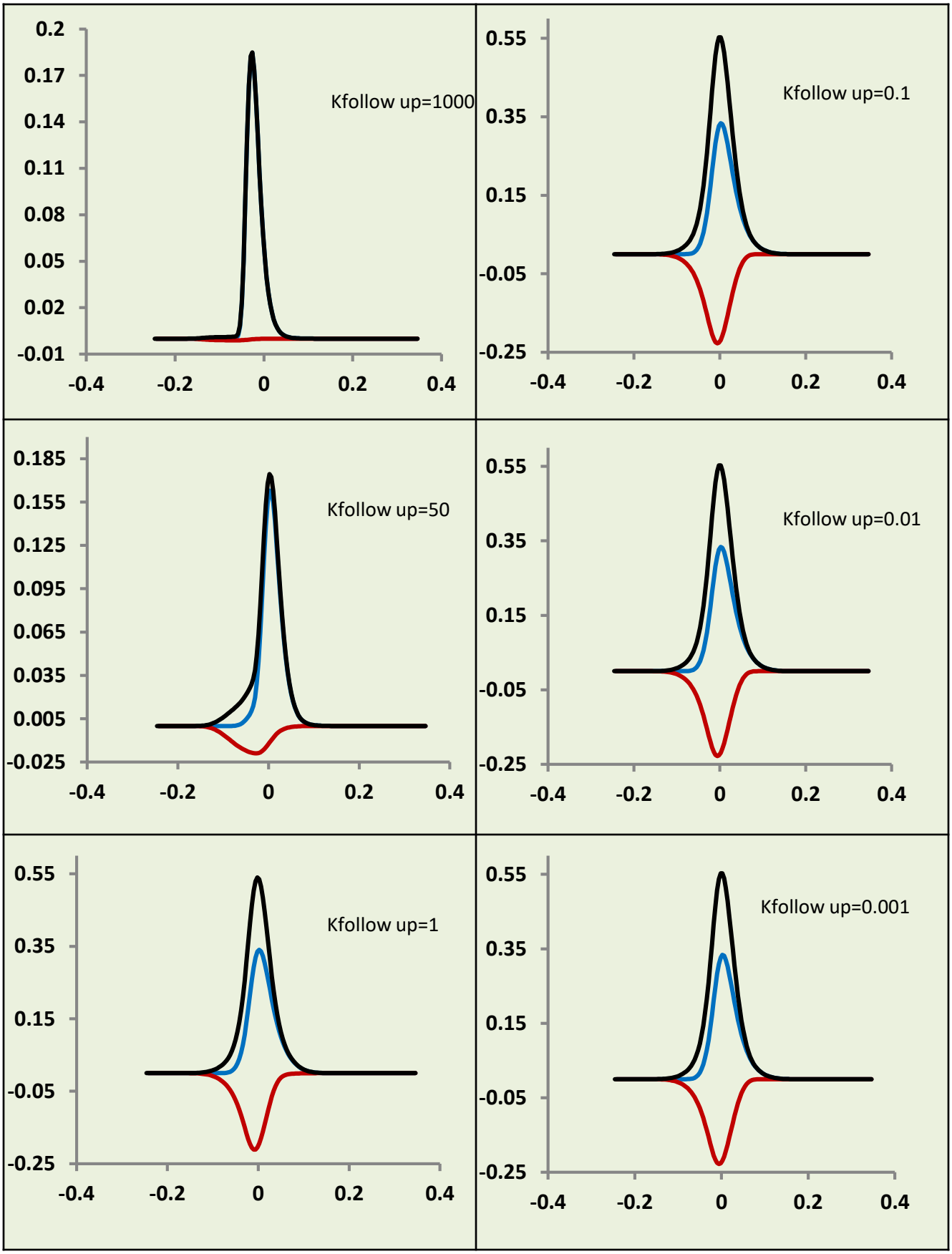
$$(I/nFS) = k_s^{\ominus}\exp(-\alpha\Phi)\,[\Gamma(\mathrm{Ox}) - \exp(\Phi)\,\Gamma(\mathrm{Red})] \quad \text{(g)}$$

Kaj сите овие 6 графици

U = Keq =10

and

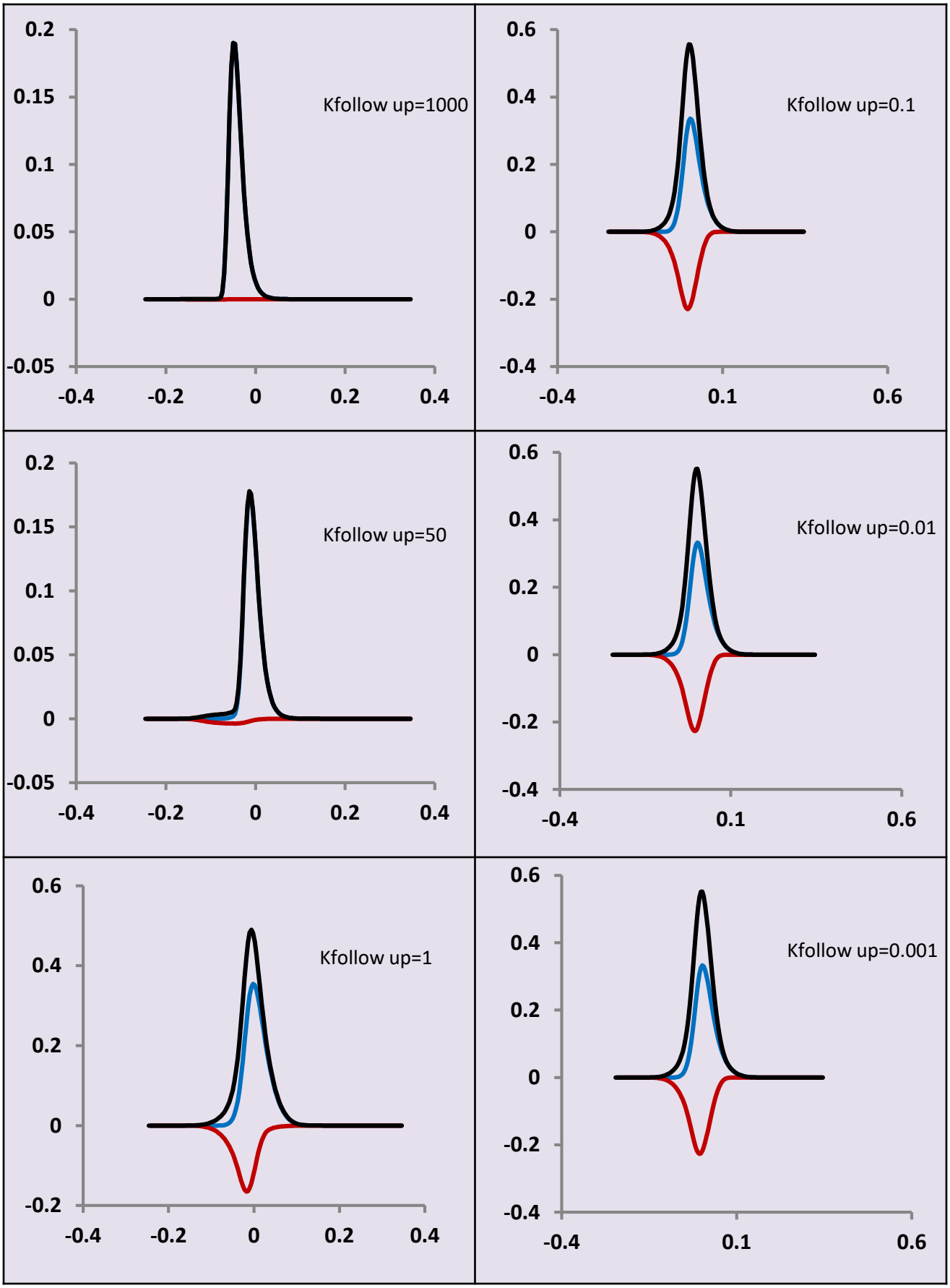
b= Kchem=10^3,50,10;1:0.01,0.001


Kfollow up=1000
Kfollow up=0.1
Kfollow up=50
Kfollow up=0.01
Kfollow up=1
Kfollow up=0.001

- Кај сите овие 6 графици

U=1

a b=1000,50,1,0.1,0.01,0.001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Kfollow up=0.1
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Kfollow up=0.01
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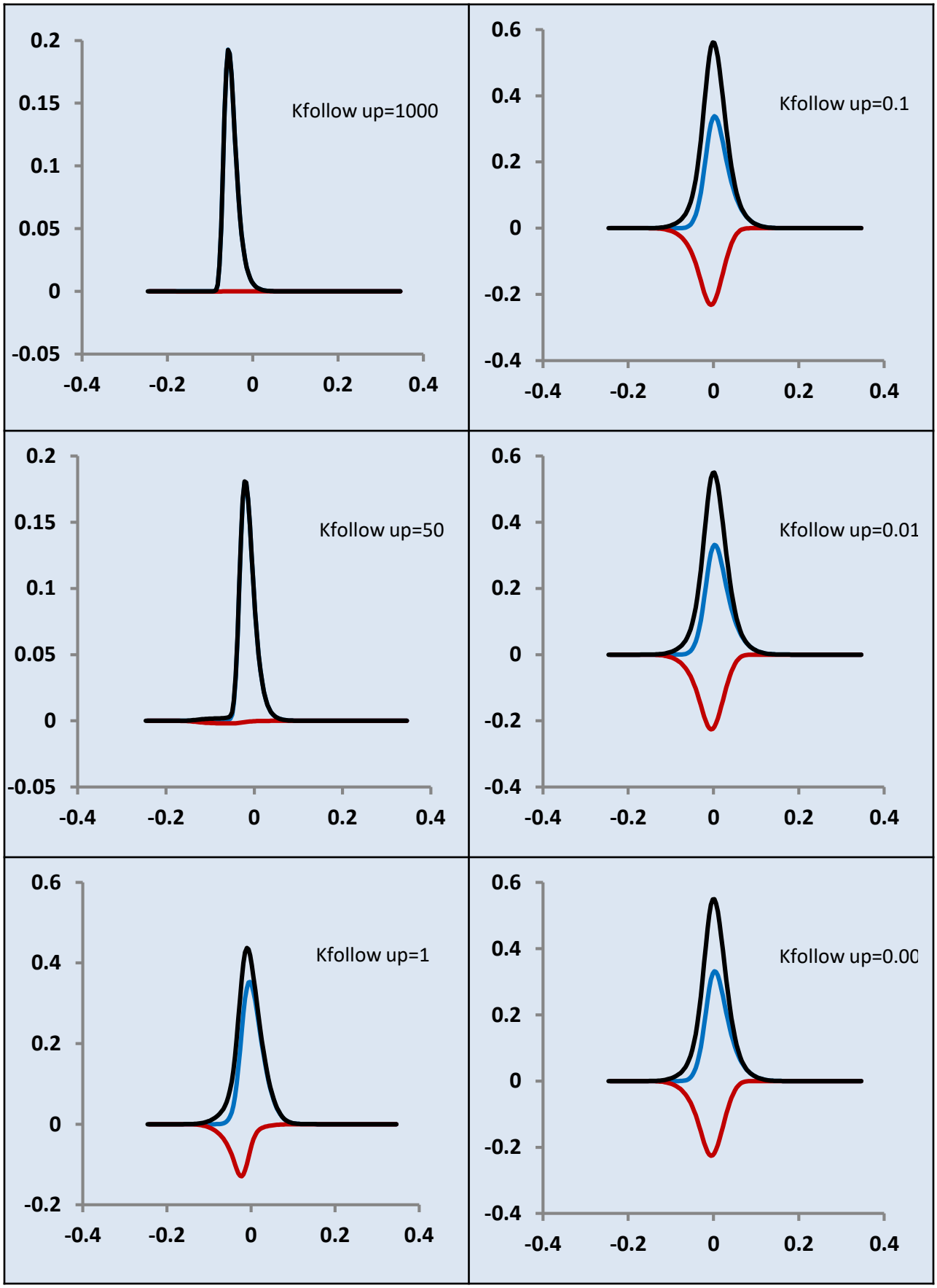
- Кај сите овие 6 графици

U=0.01

а b=1000,50,1,0.1,0.01,0.001


Kfollow up=1000
Kfollow up=0.1
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$Ks=10^{1,25}$

U=1000

b=0.001

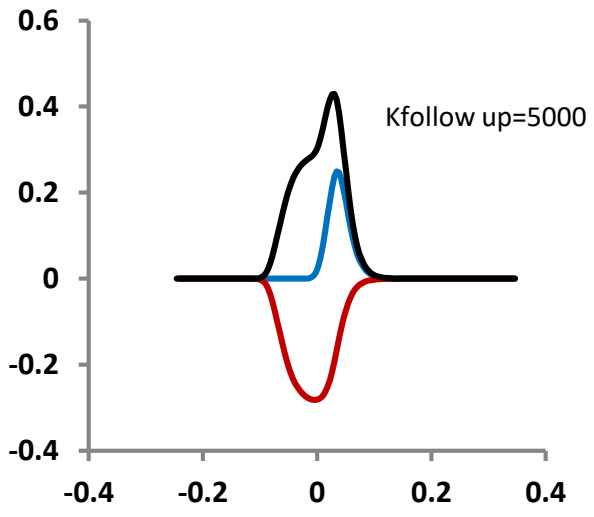
0.01

0.1

1

50

1000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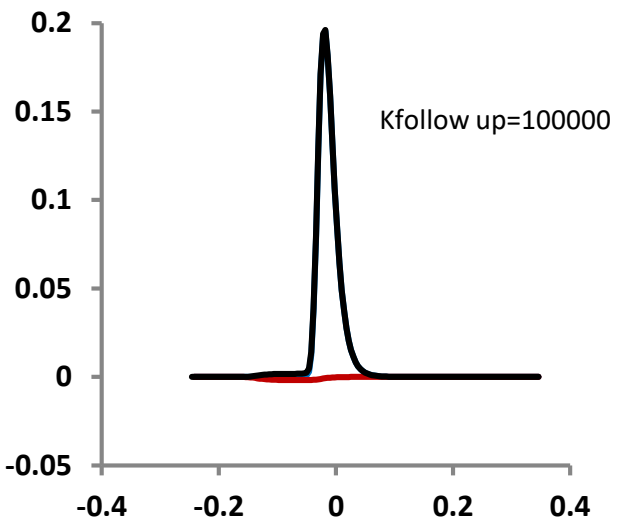
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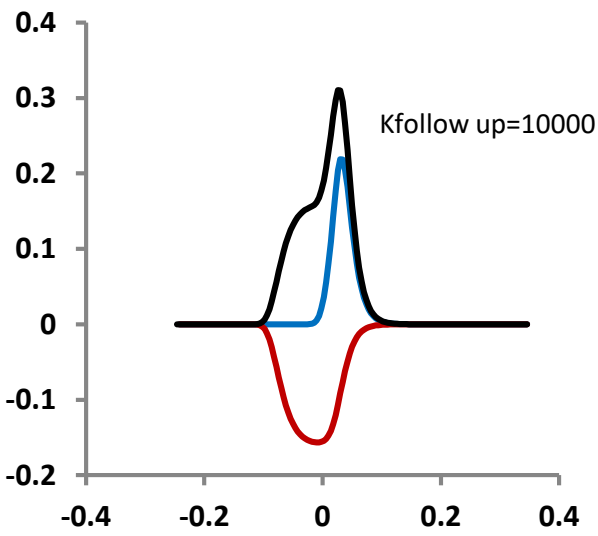
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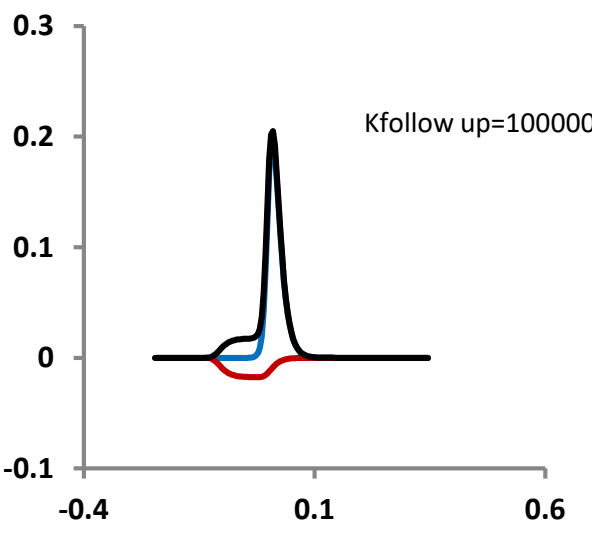
Kfollow up=10000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0.6
Kfollow up=100000

$Ks=10^{1,25}$

$U=10$

b=0.001

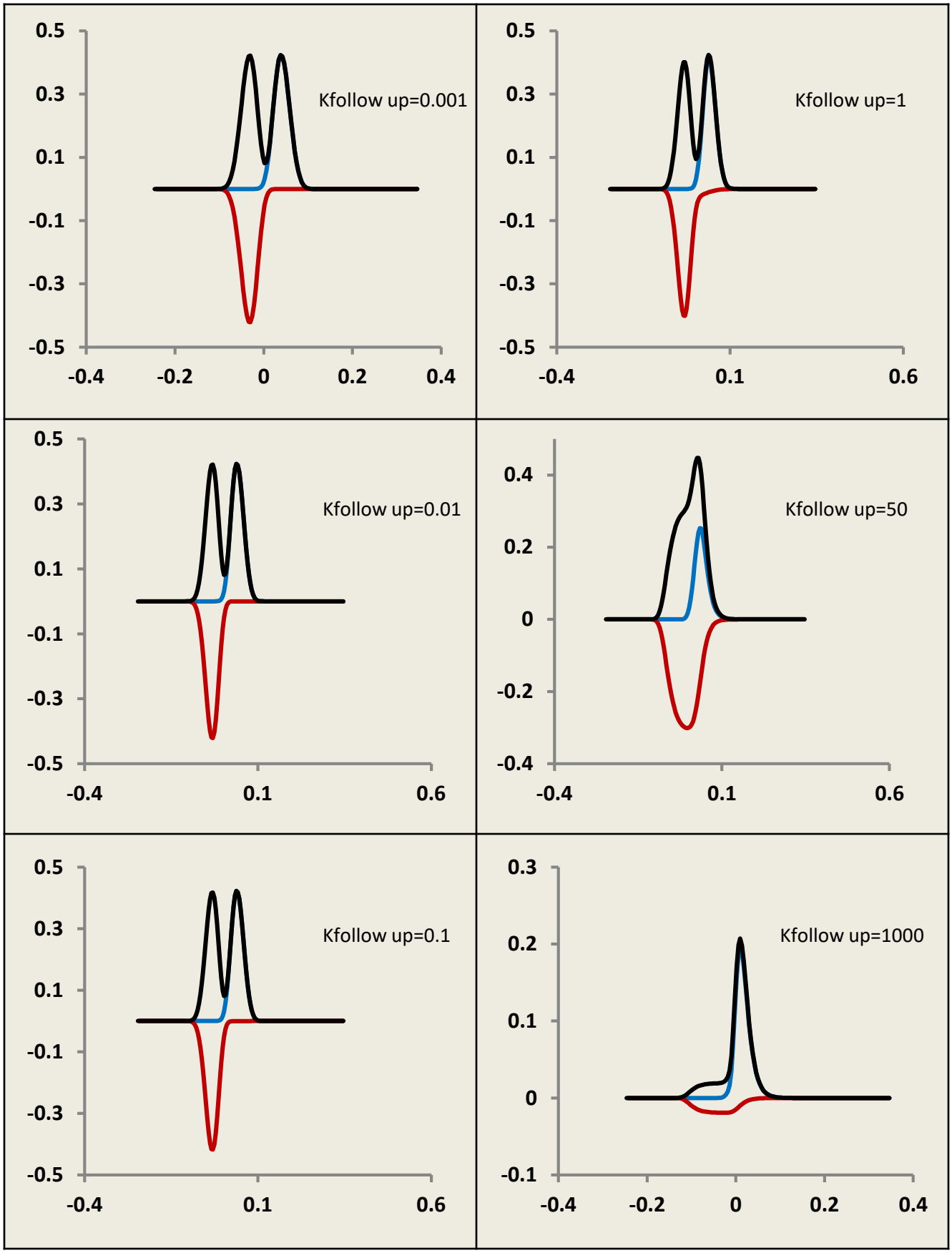
0.01

0.1

1

50

1000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Kfollow up=0.01
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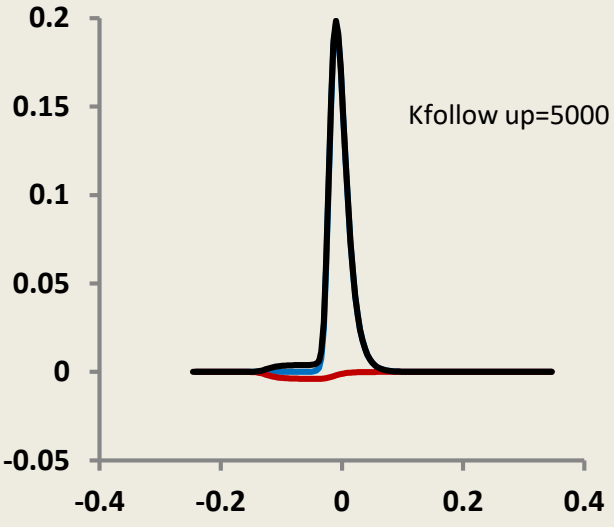
Kfollow up=0.1
Kfollow up=1000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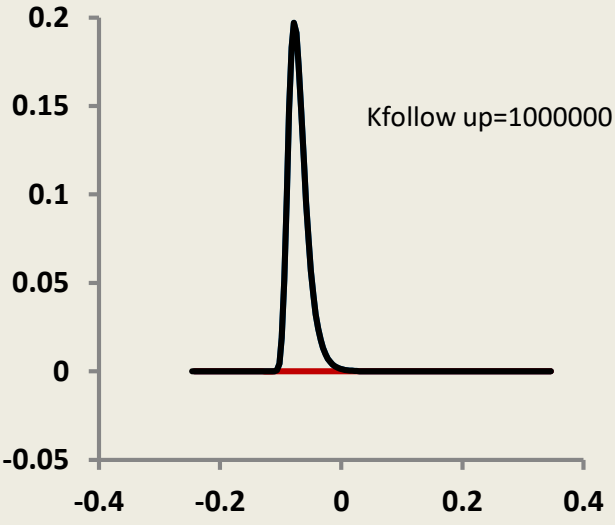
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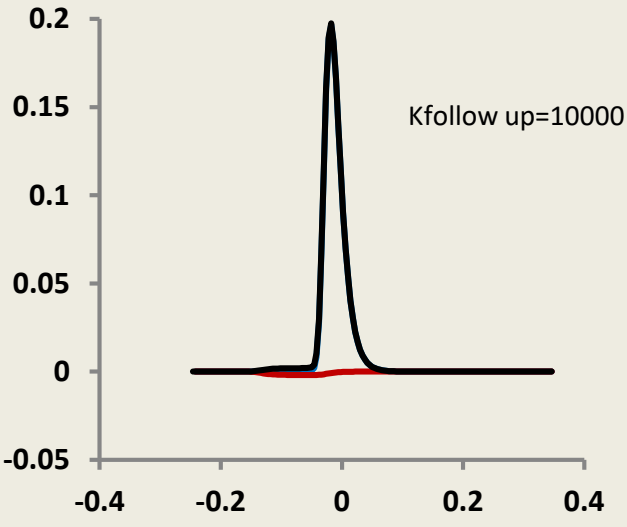
Kfollow up=1000000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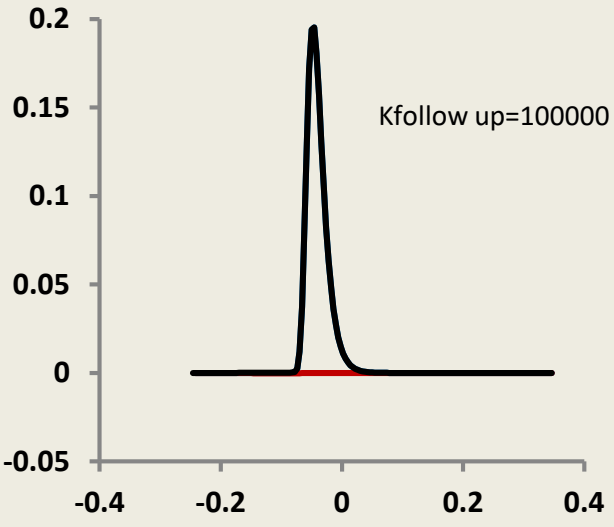
Kfollow up=10000


0.2
0.15
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0
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-0.2
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Kfollow up=100000

$Ks=10^{1,25}$

$U=1$

b=0.001

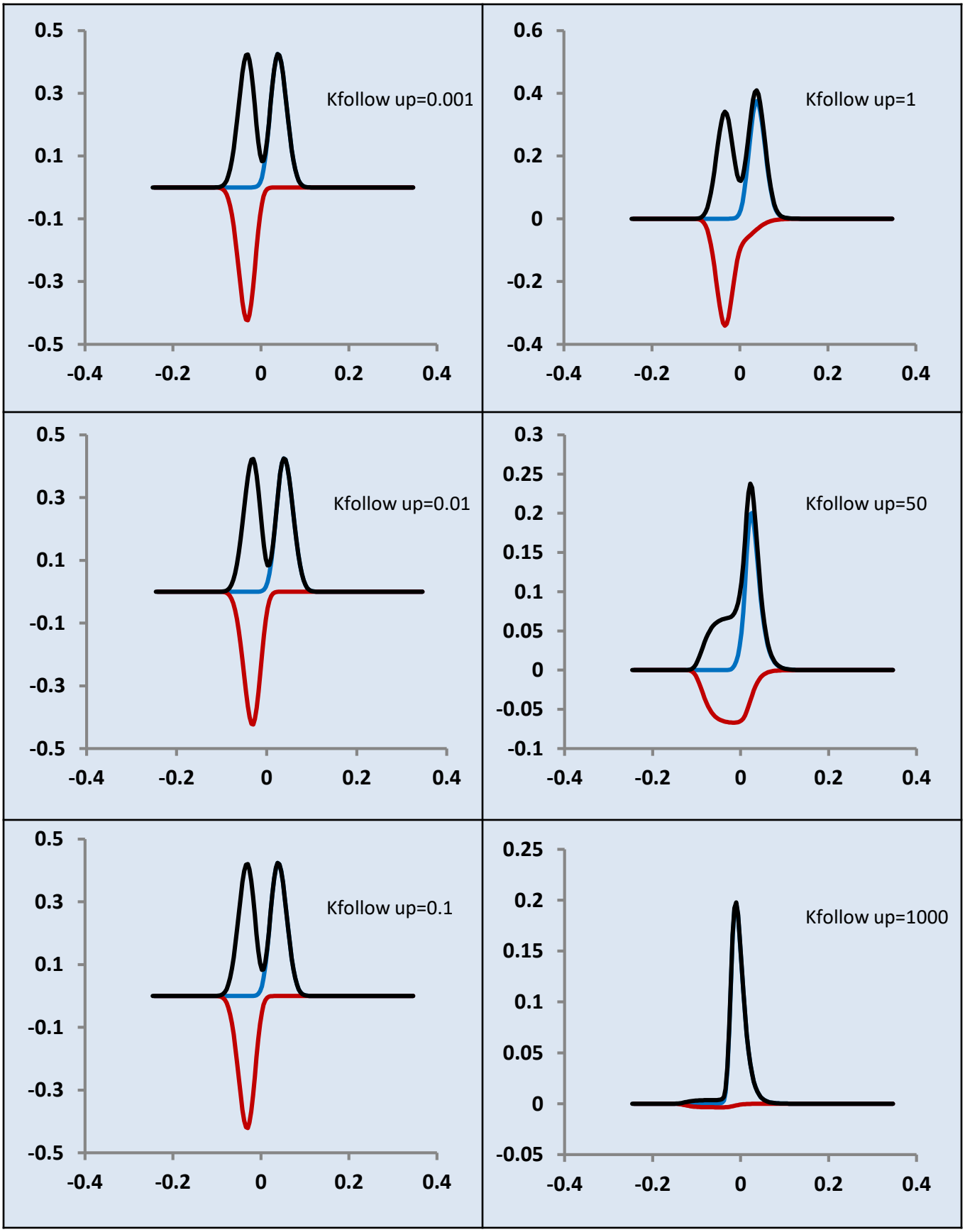
0.01

0.1

1

50

1000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Kfollow up=1
Kfollow up=0.01
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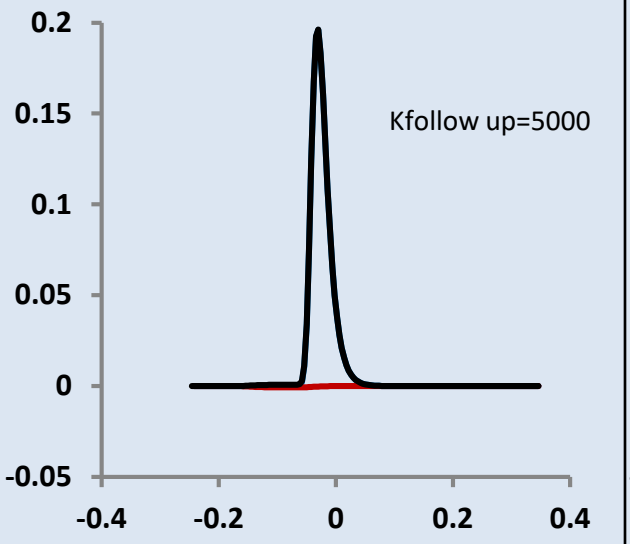
Kfollow up=0.1
Kfollow up=1000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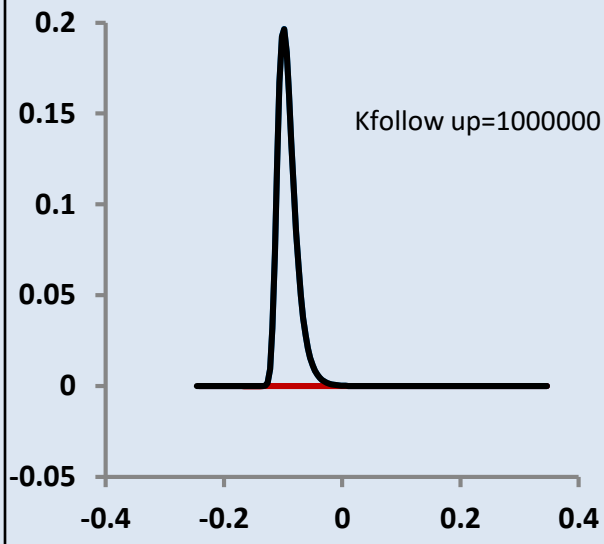
Kfollow up=5000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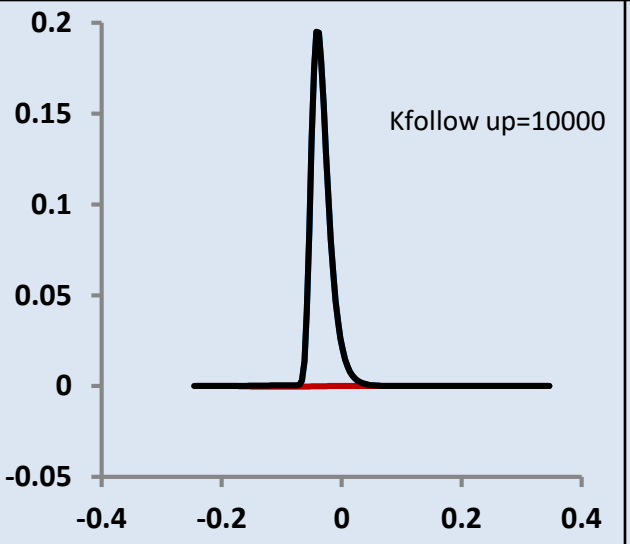
Kfollow up=1000000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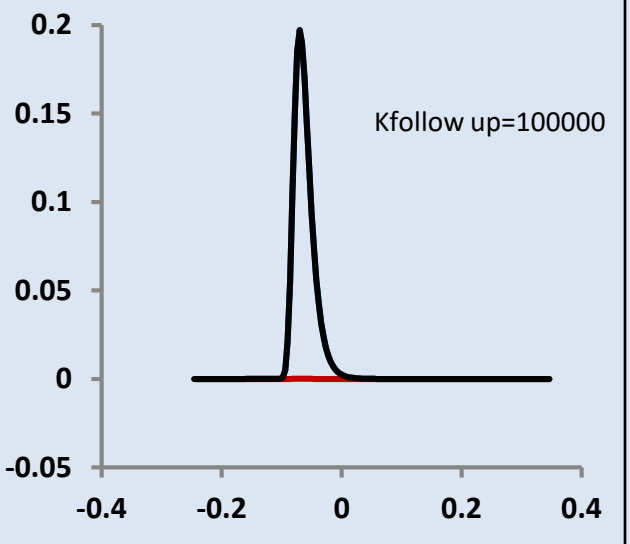
Kfollow up=10000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-0.4
-0.2
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Kfollow up=100000

$Ks=10^{1,25}$

$U=0.01$

b=0.001

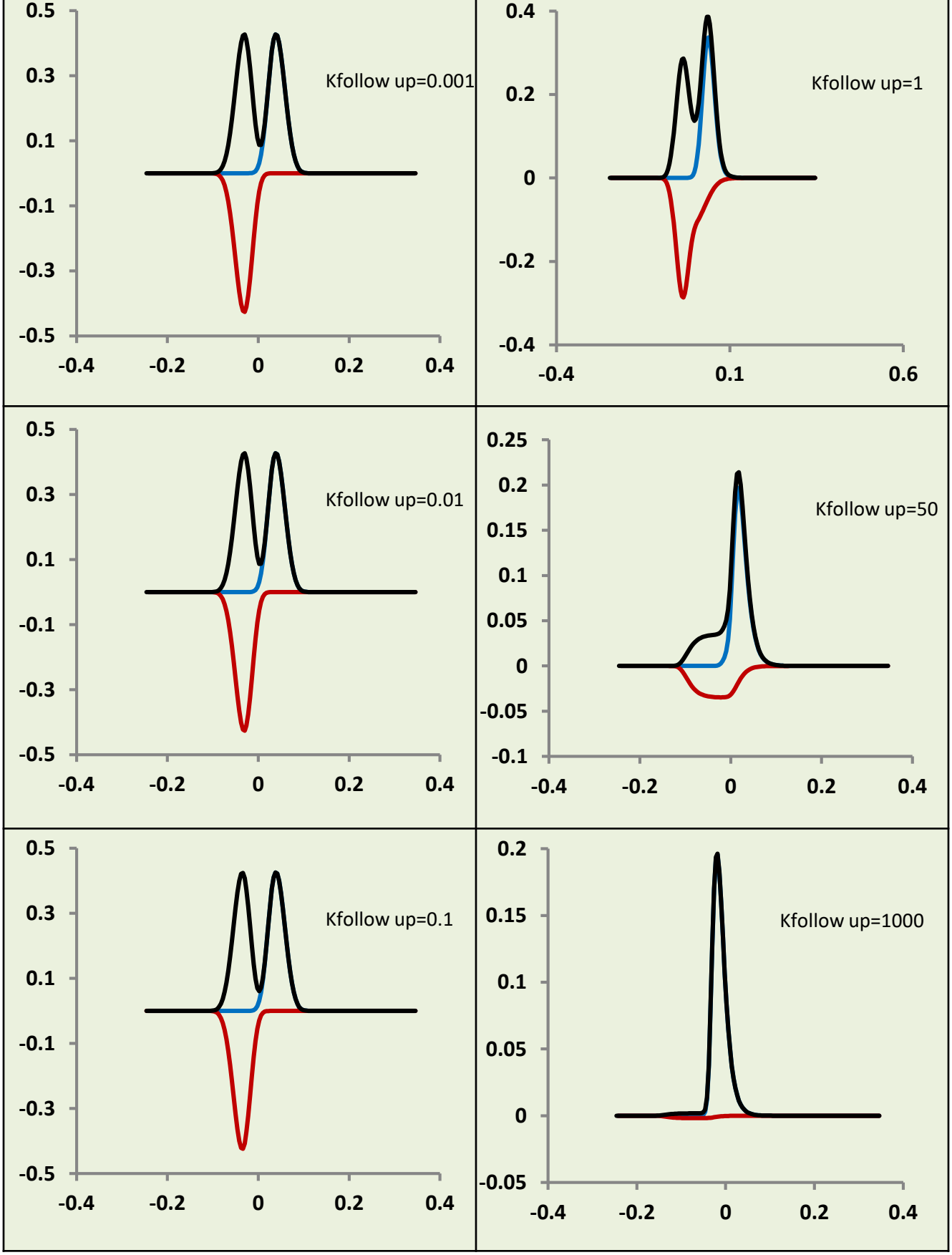
0.01

0.1

1

50

1000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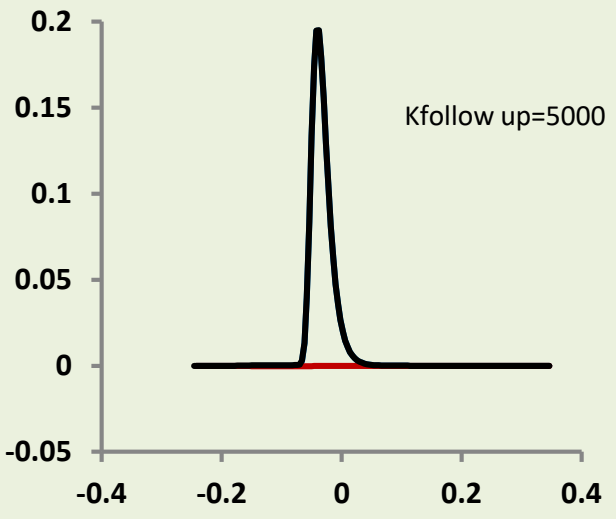
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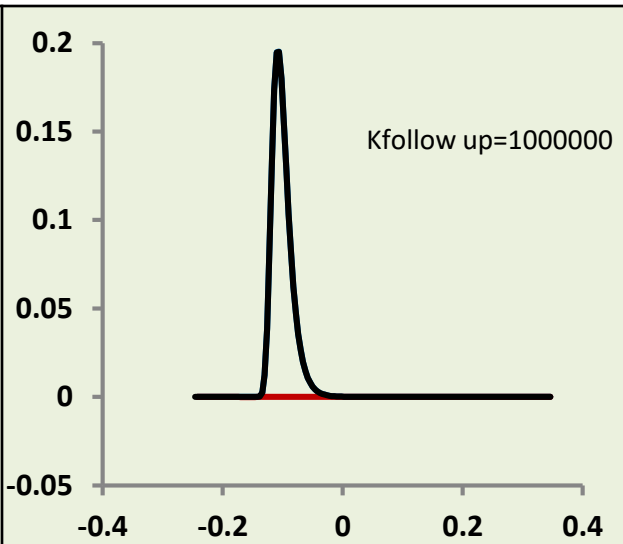
Kfollow up=5000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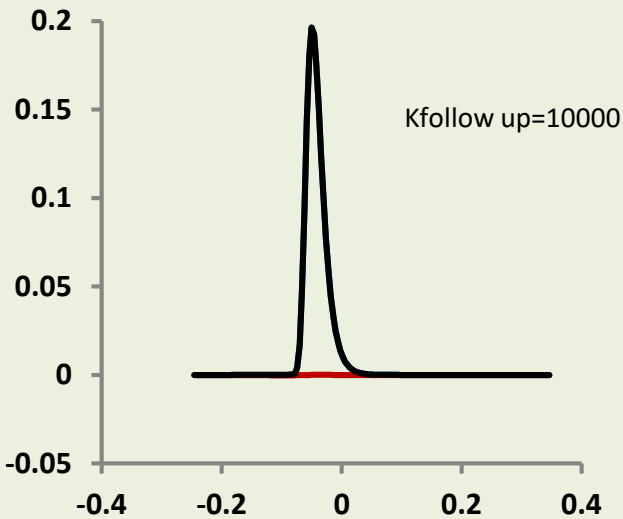
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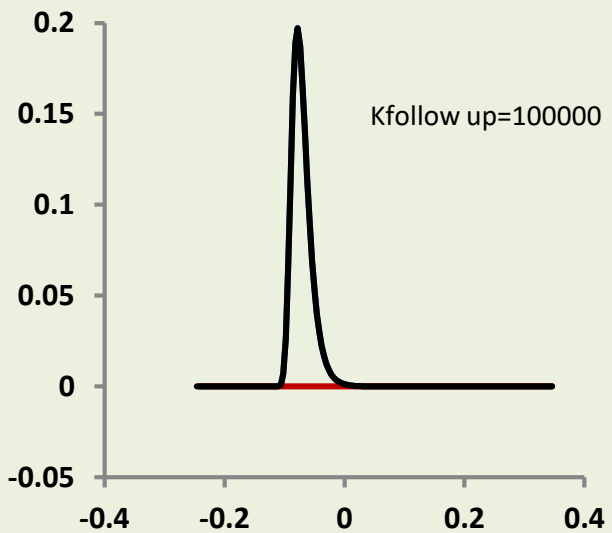
Kfollow up=10000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Kfollow up=100000

$Ks=10^0$

$U=1000$

b=0.001

0.01

0.1

1

50

1000

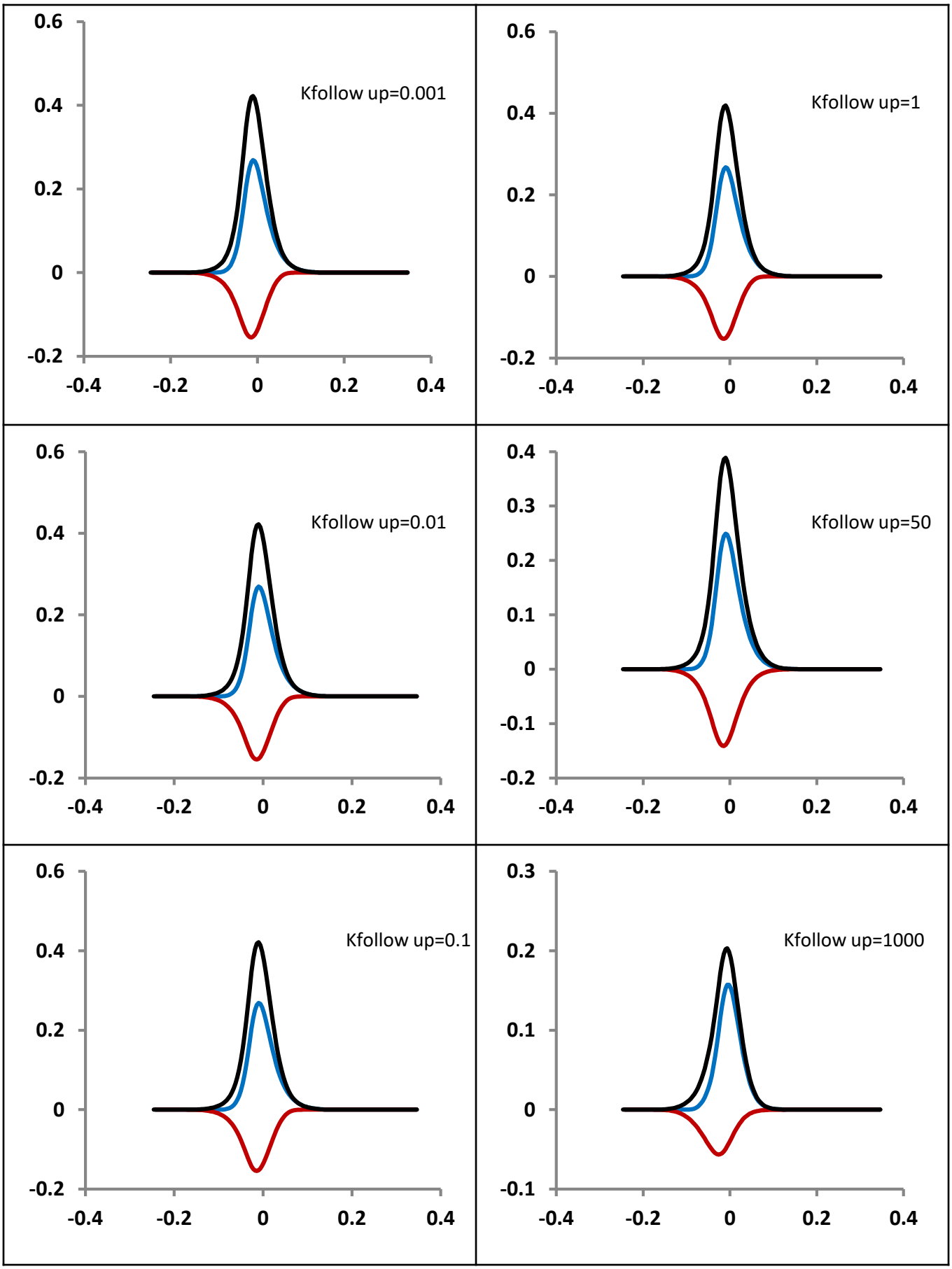
5000

10000

100000

1000000

- Epsilon 10^3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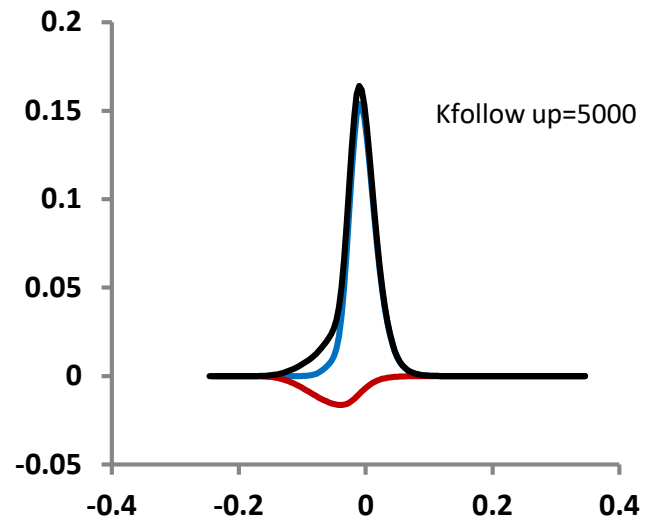
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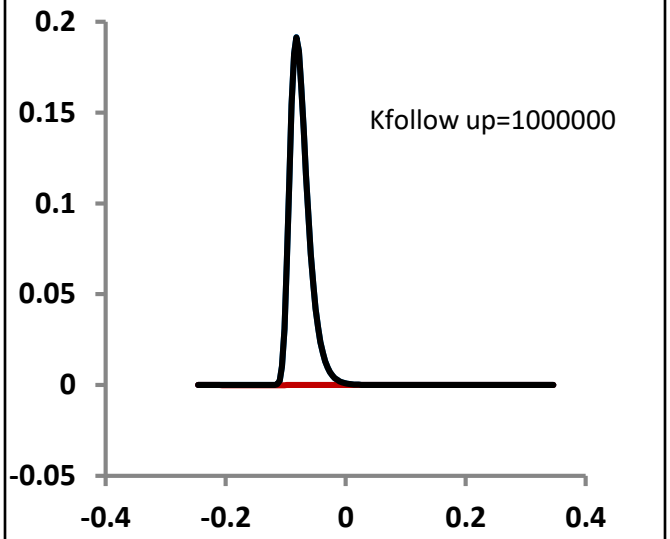
Kfollow up=5000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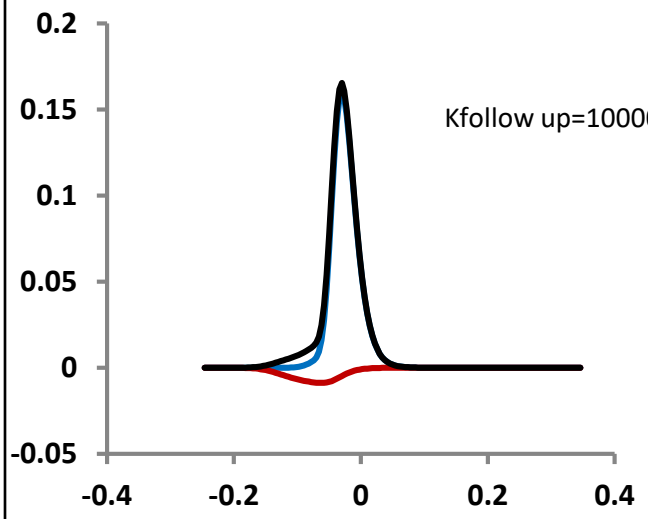
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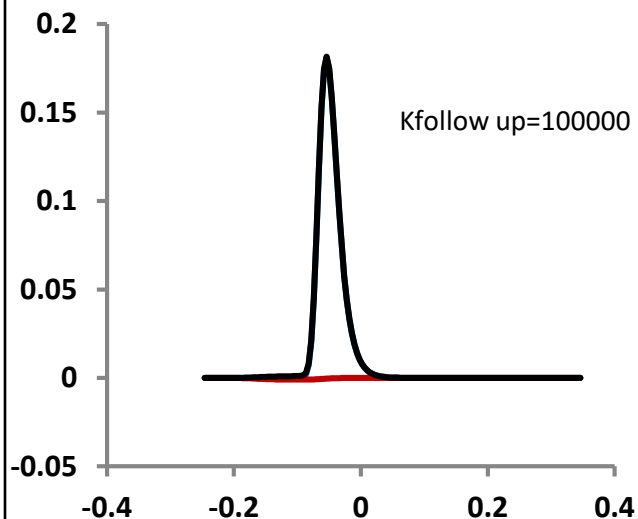
Kfollow up=10000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-0.4
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Kfollow up=100000

$Ks=10^0$

U=1

b=0.001

0.01

0.1

1

50

1000

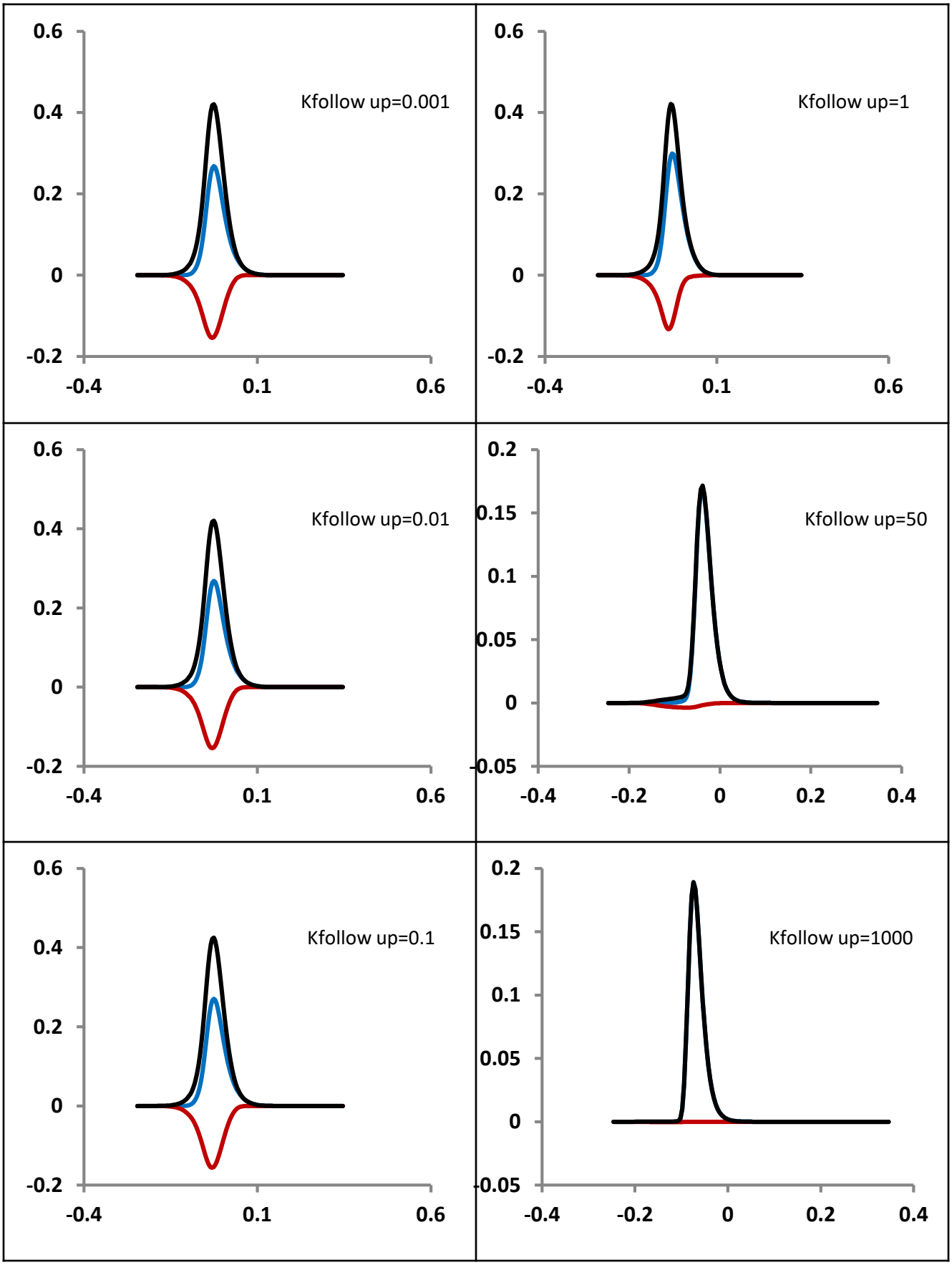
5000

10000

100000

1000000

- Epsilon 10^3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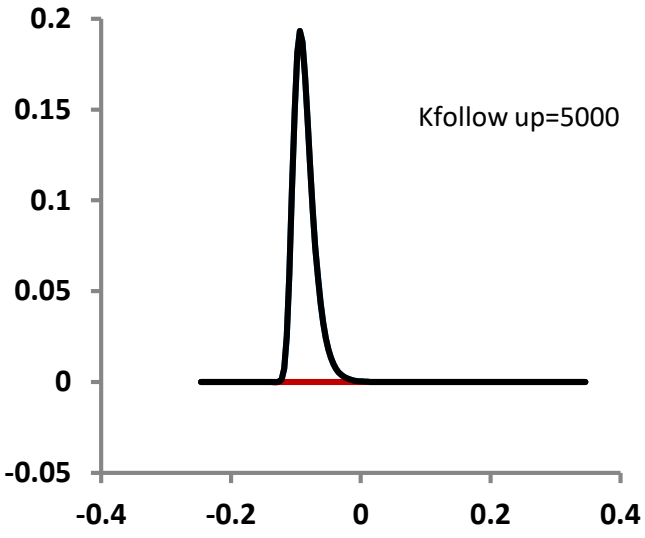
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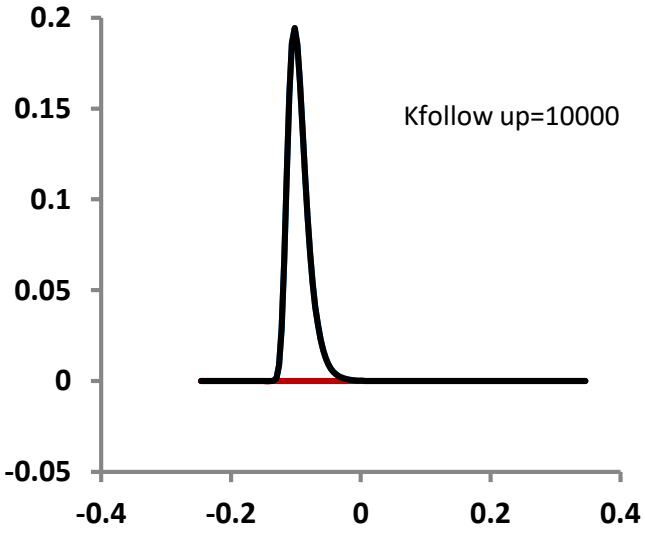
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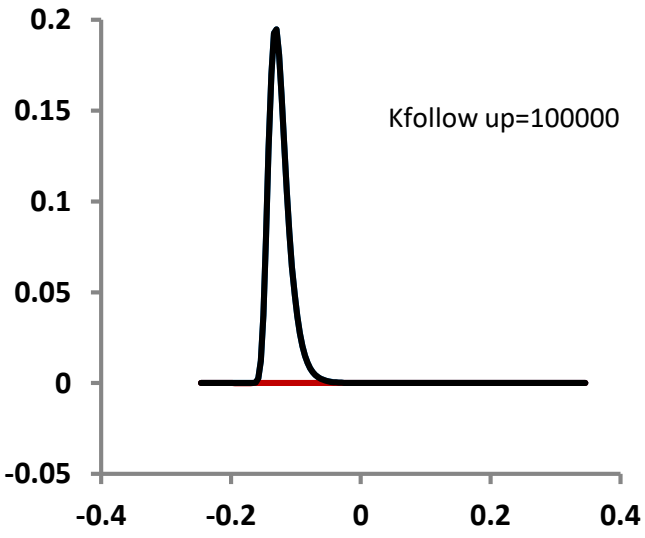
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Kfollow up=100000

$Ks=10^0$

$U=0.01$

b=0.001

0.01

0.1

1

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1000

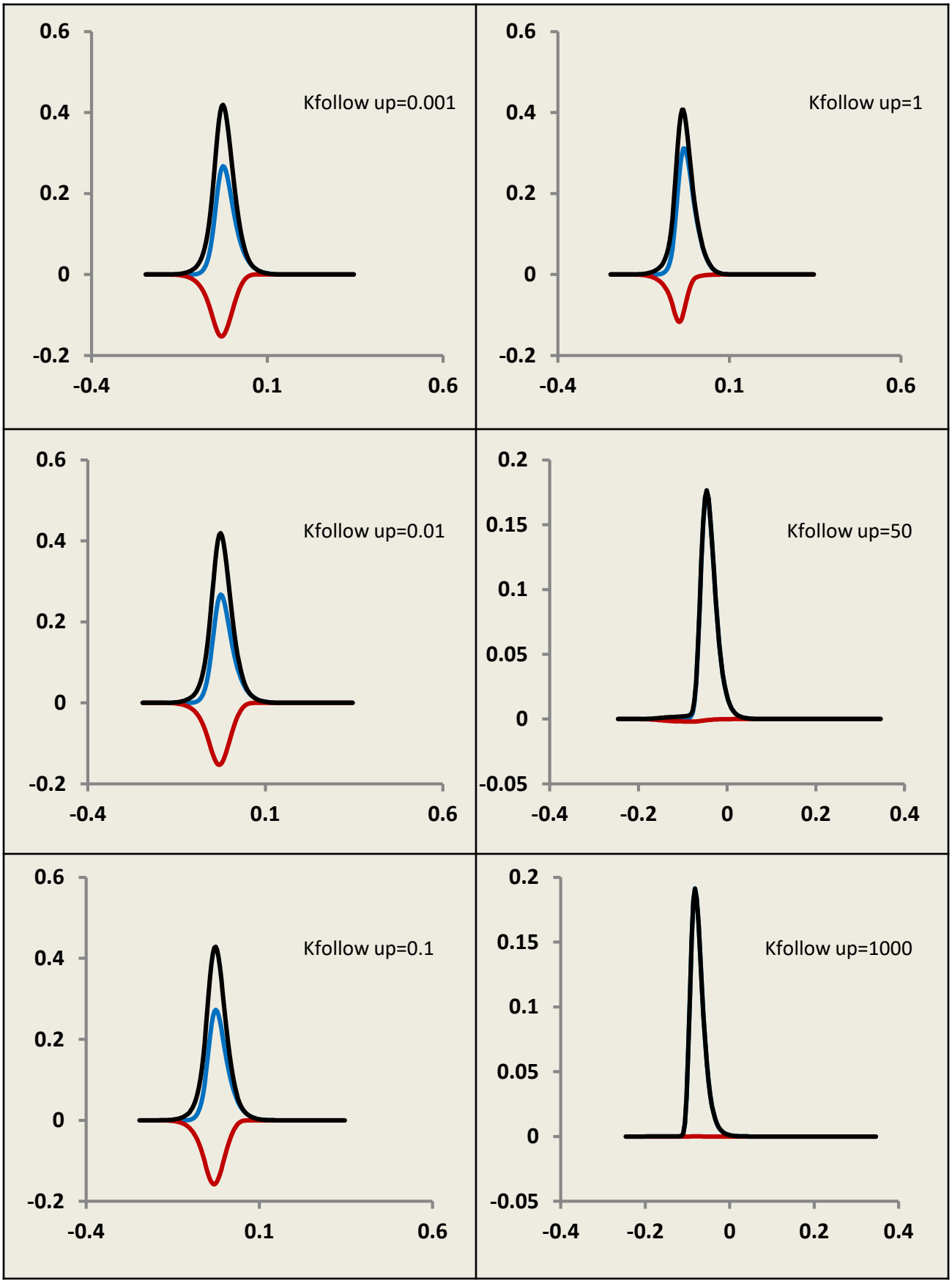
5000

10000

100000

1000000

- Epsilon 10^3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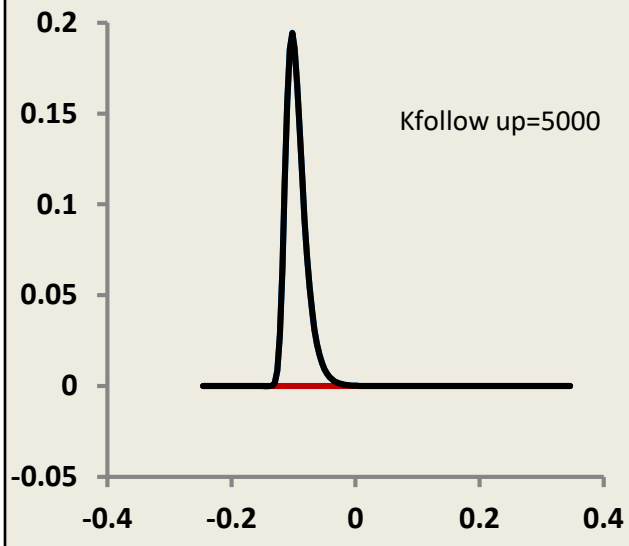
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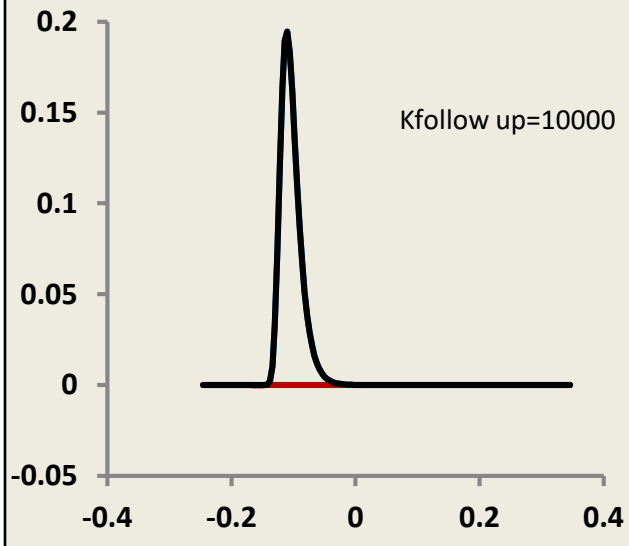
Kfollow up=5000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0.4
Kfollow up=10000

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b=0.001

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0.1

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10000

100000

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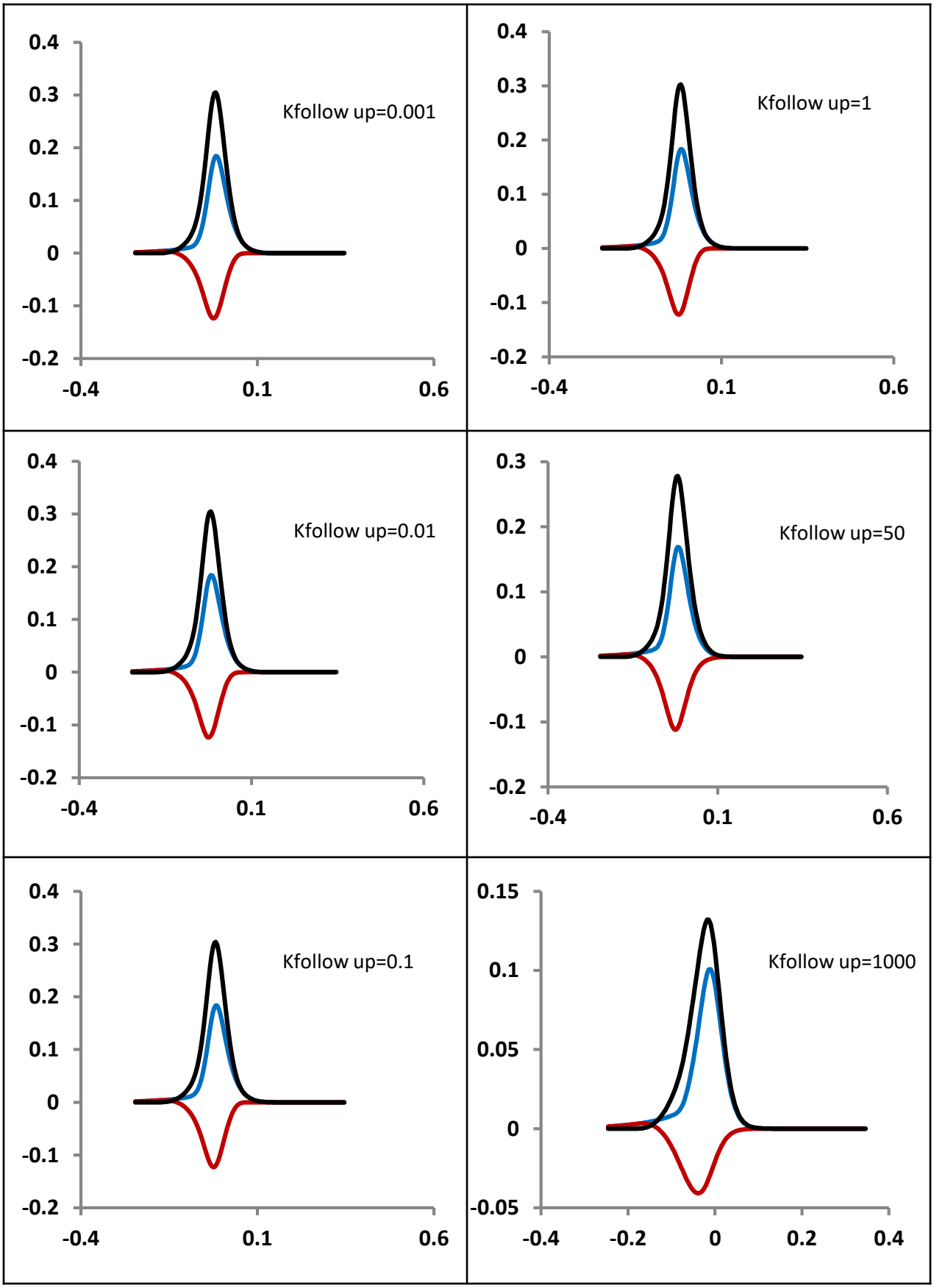
- Epsilon 10^0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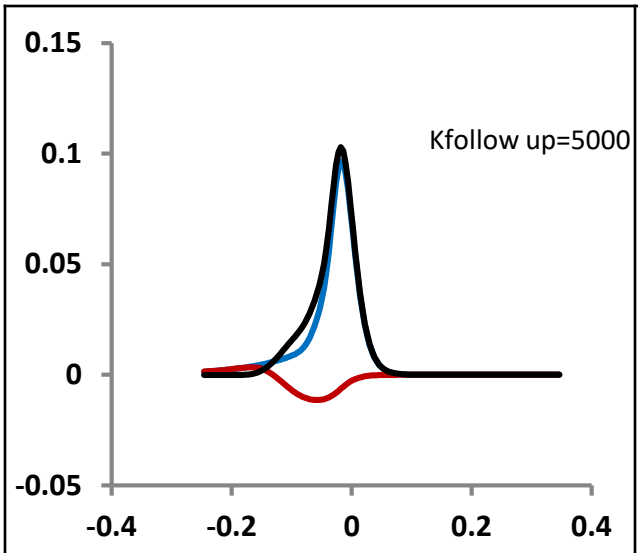
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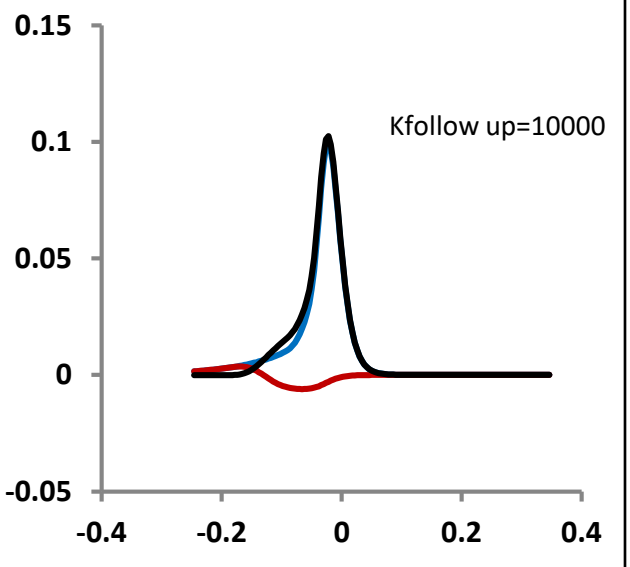
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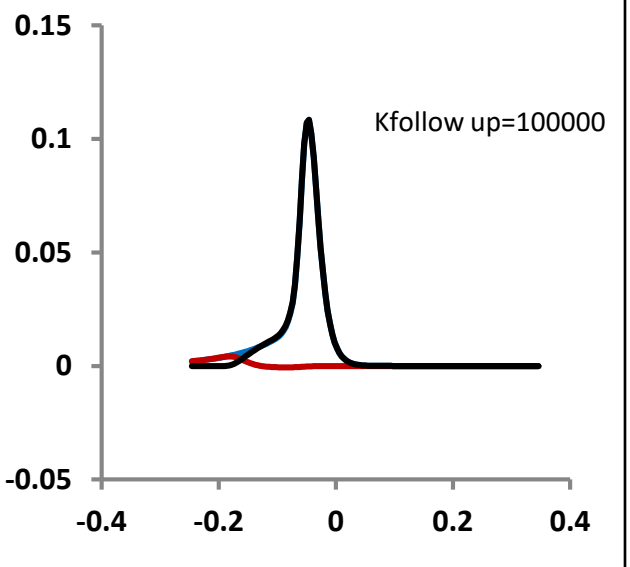
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b=0.001

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0.1

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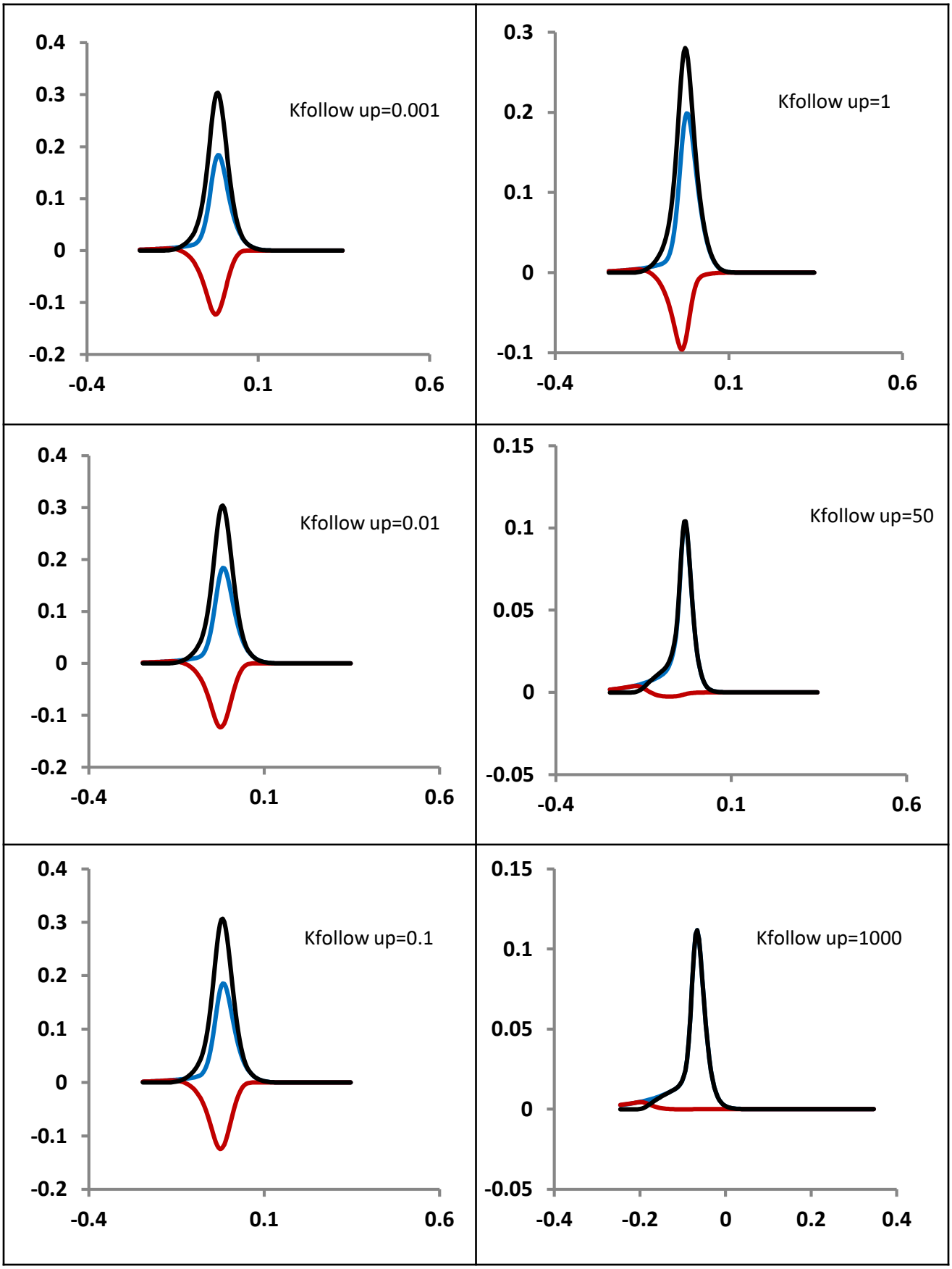
- Epsilon 10^0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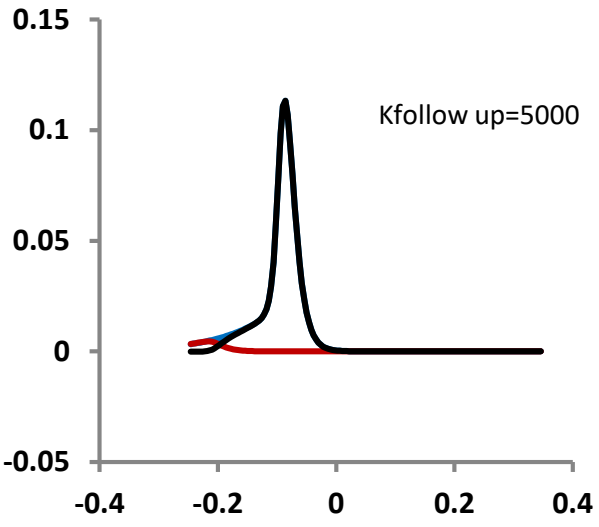
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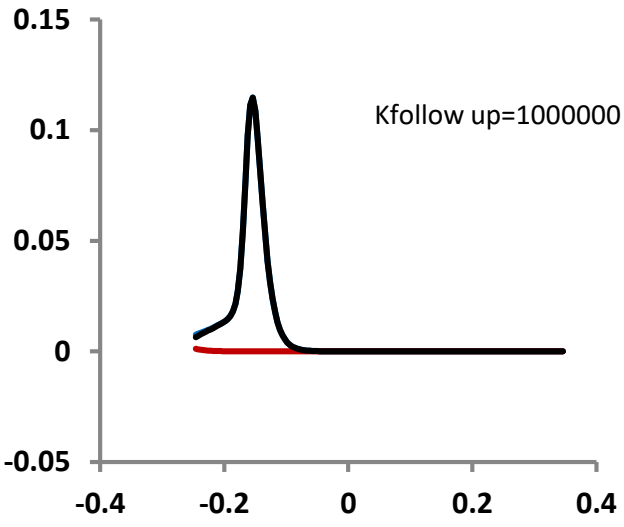
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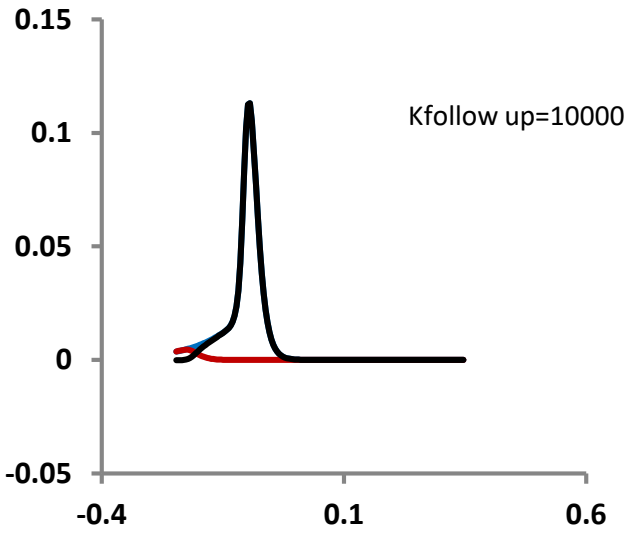
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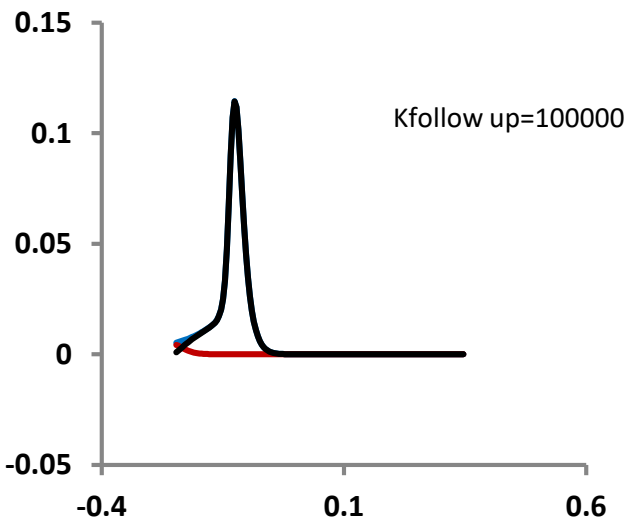
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b=0.001

0.01

0.1

1

50

1000

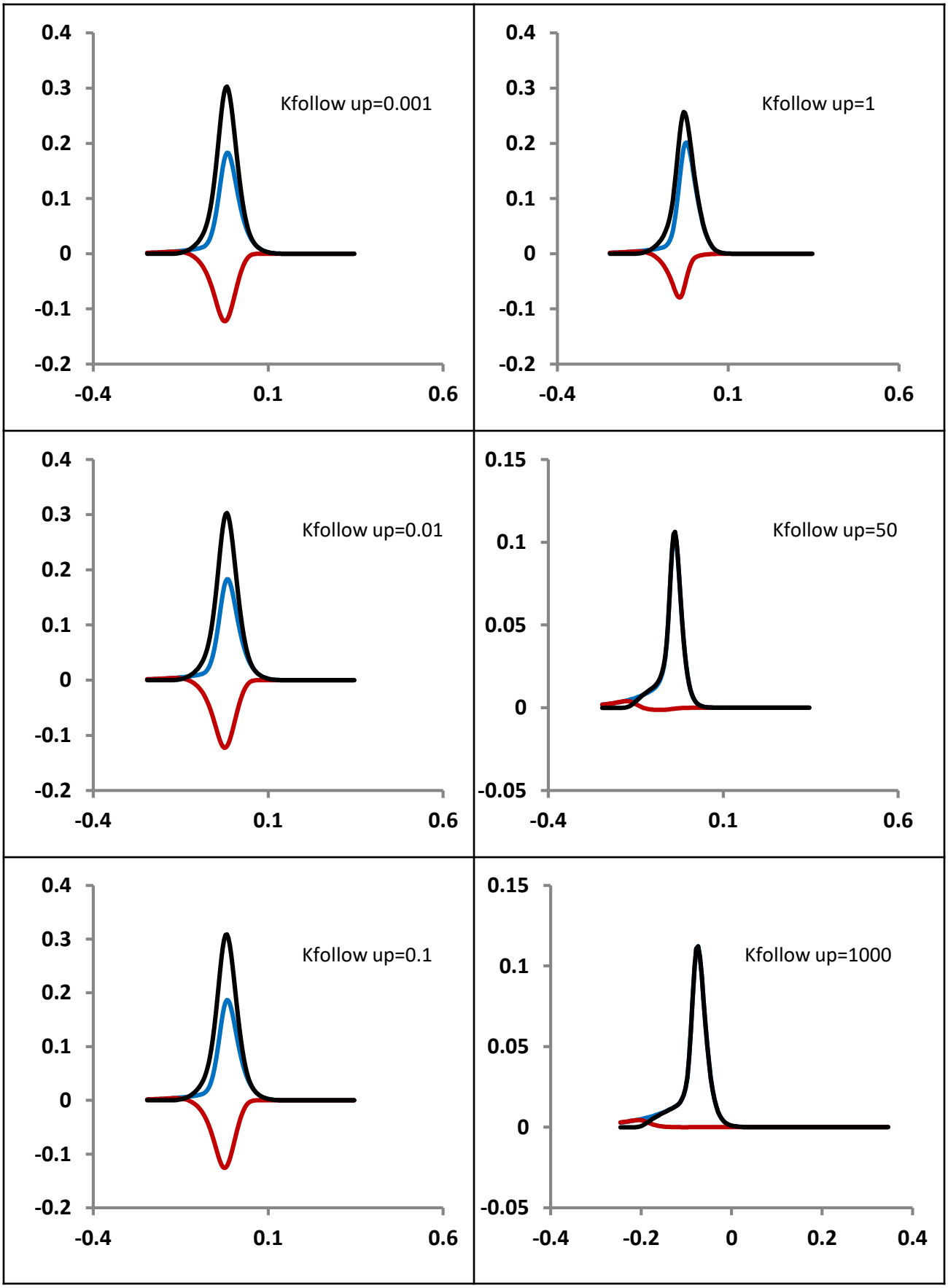
5000

10000

100000

1000000

- Epsilon 10^0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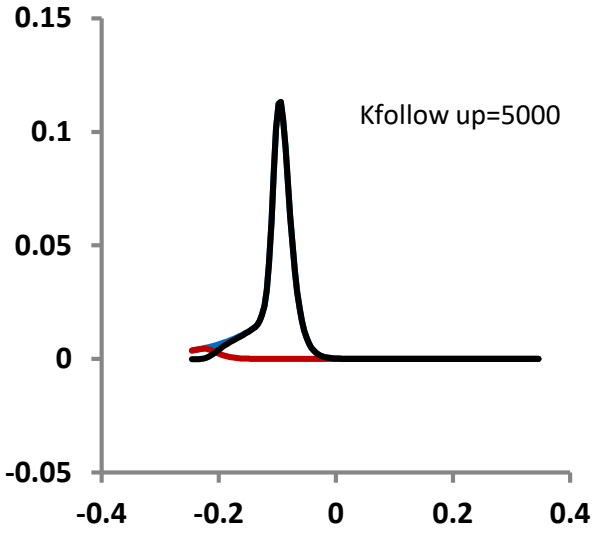
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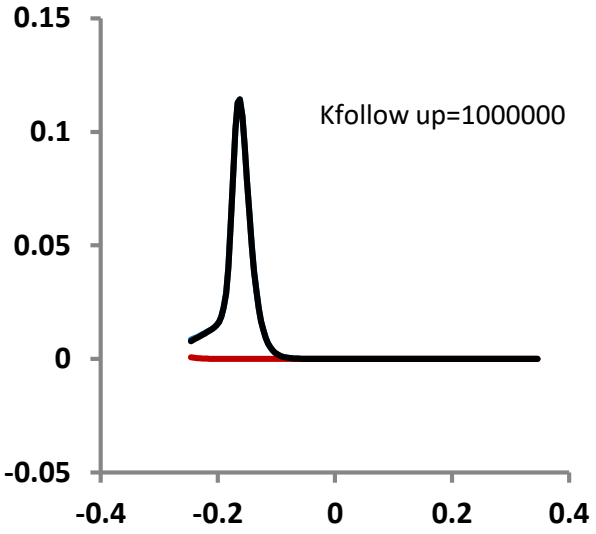
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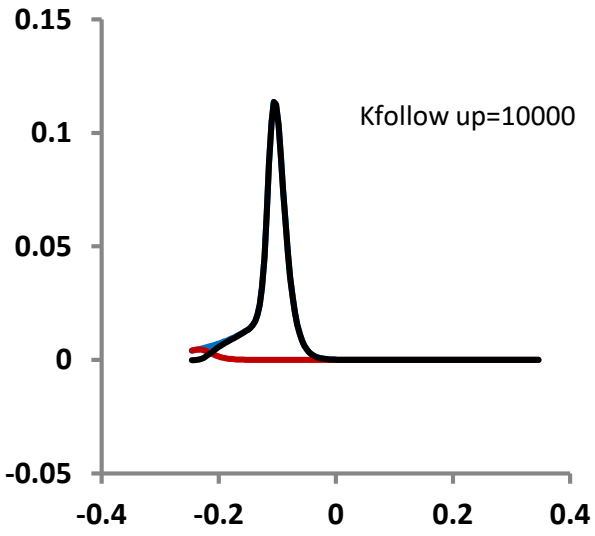
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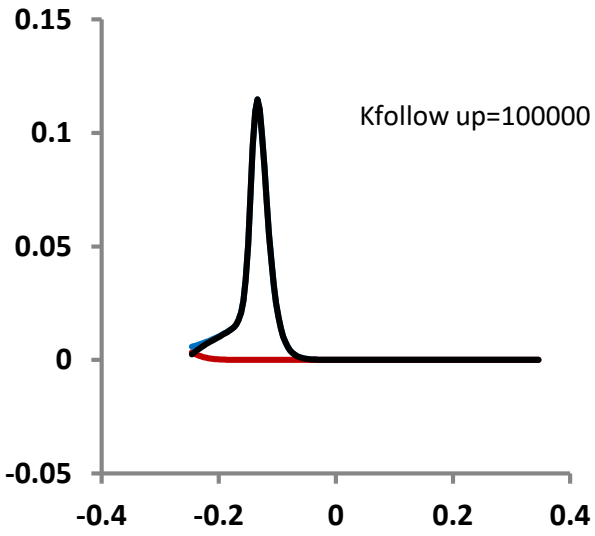
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0.4
Kfollow up=100000

Ks=10^0

U=1000

b=0.001

0.01

0.1

1

50

1000

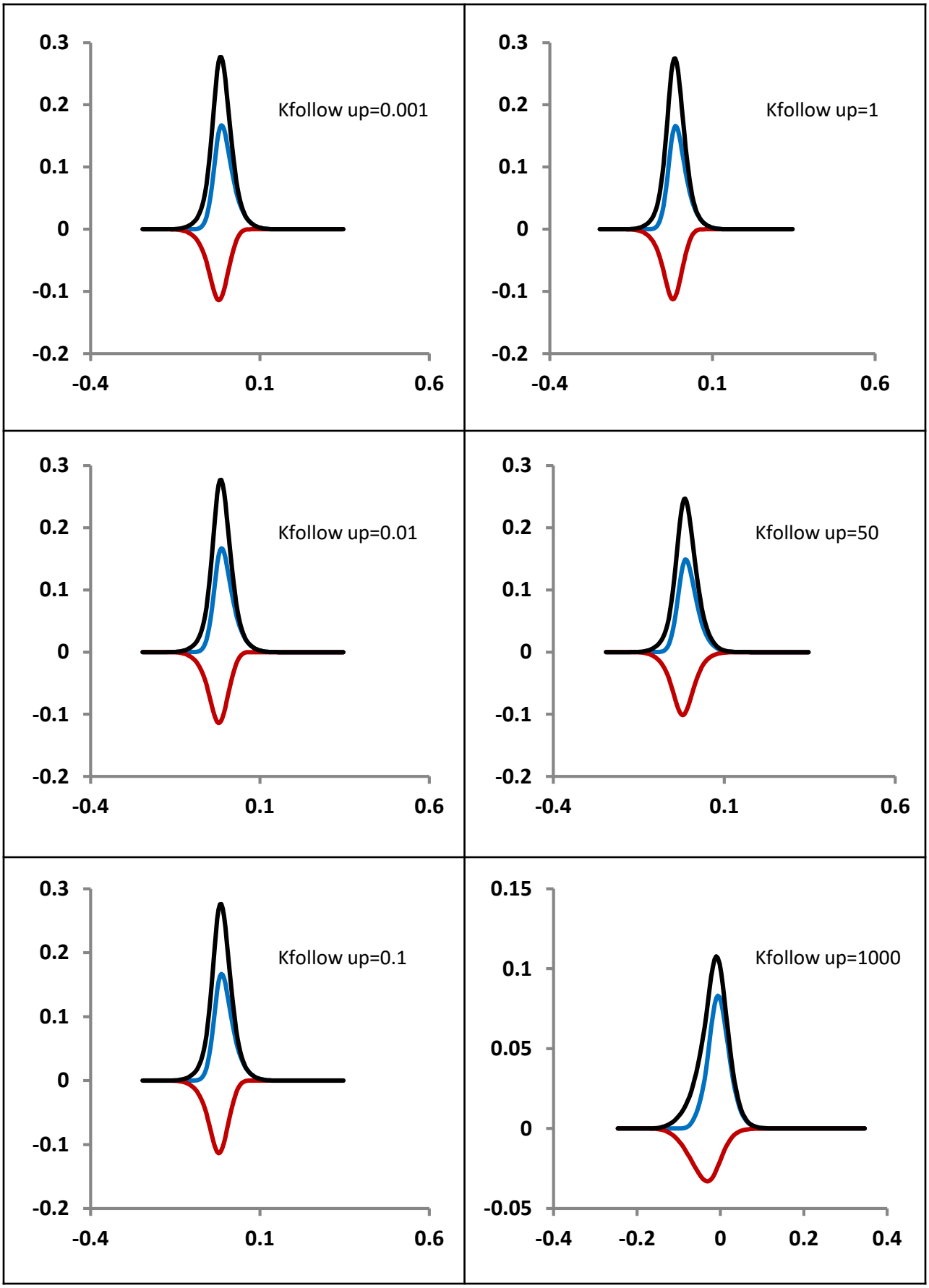
5000

10000

100000

1000000

- Epsilon 10^{minus3}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Kfollow up=0.1
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0.2
0.1
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0.6
0.15
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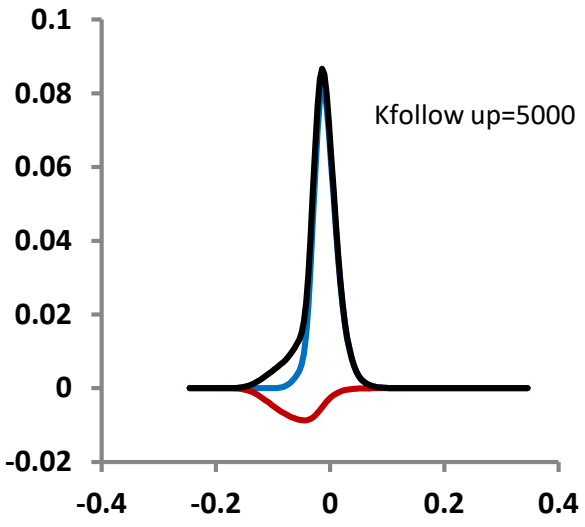
-0.05
-0.2
0.2
0.4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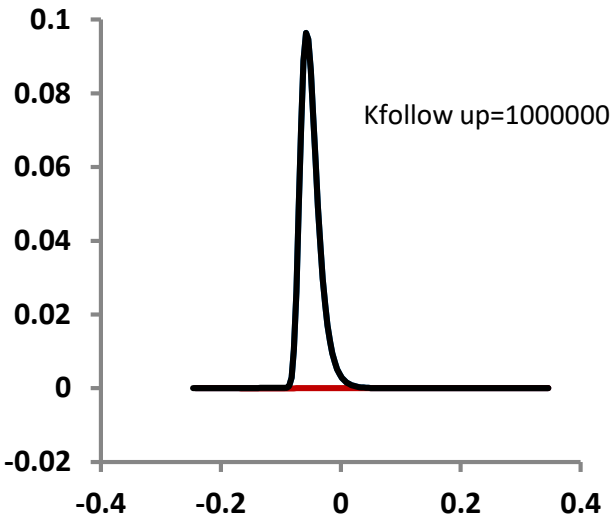
0
0.2
0.4
Kfollow up=5000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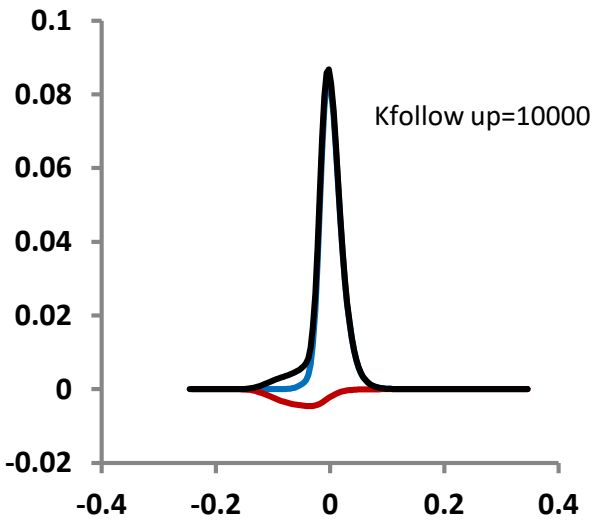
Kfollow up=1000000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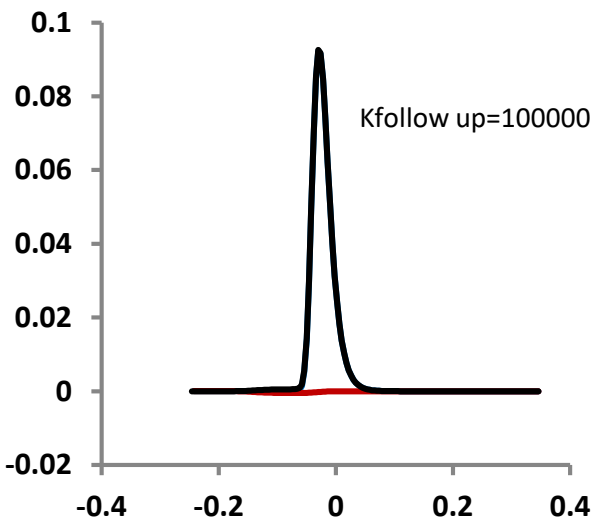
0.4
Kfollow up=10000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0.06
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0.02
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-0.02
-0.4
-0.2
0
0.2
0.4
Kfollow up=100000

$Ks=10^0$

U=1

b=0.001

0.01

0.1

1

50

1000

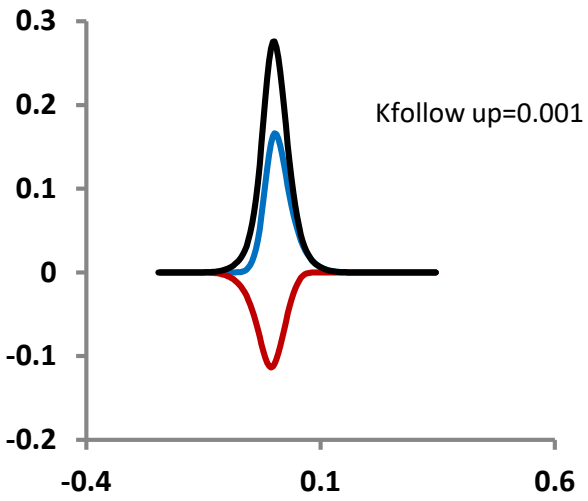
5000

10000

100000

1000000

- Epsilon 10^{minus3}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0
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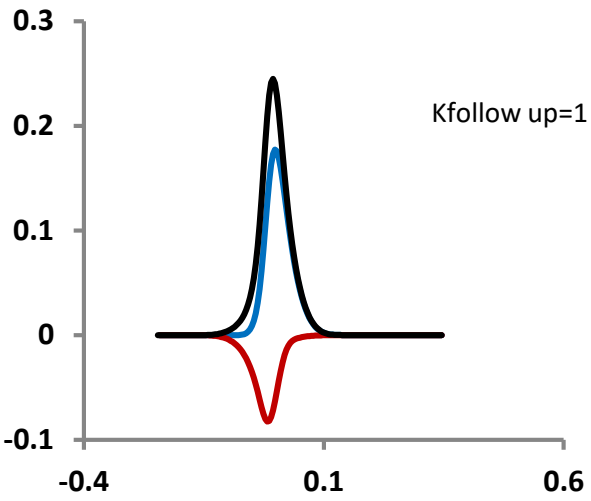
-0.2
-0.4
0.1
0.6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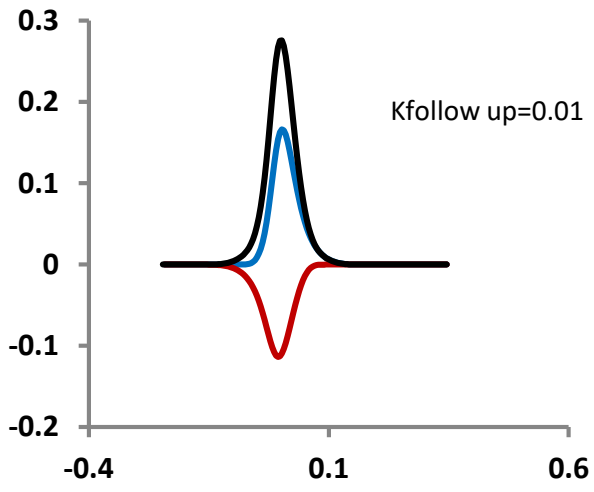
0.3
0.2
0.1
0
-0.1
-0.4
0.1
0.6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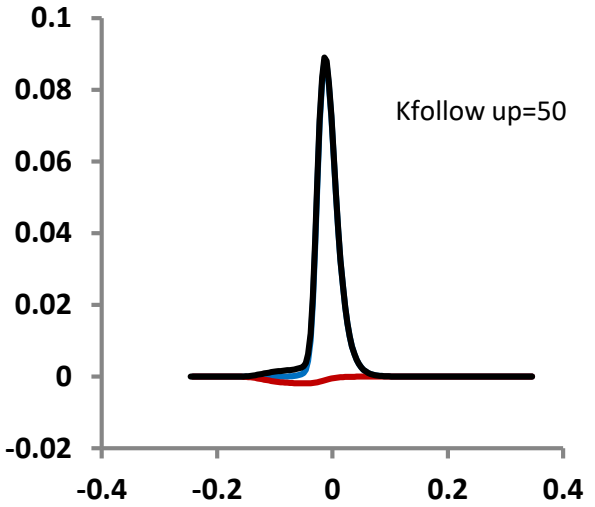
0.2
0.1
0
-0.1
-0.2
-0.4
0.1
0.6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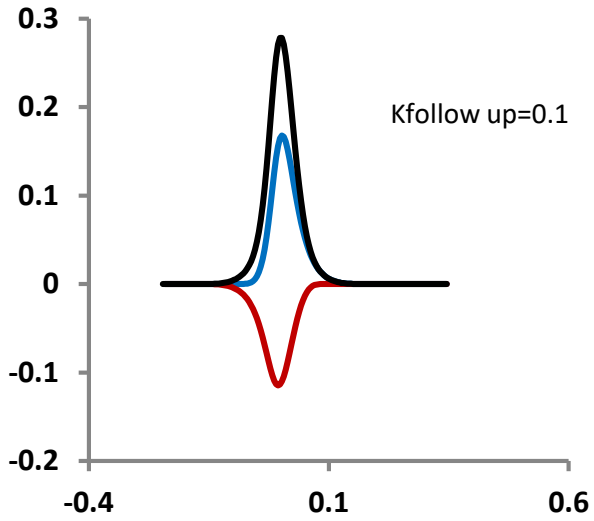
0.4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0
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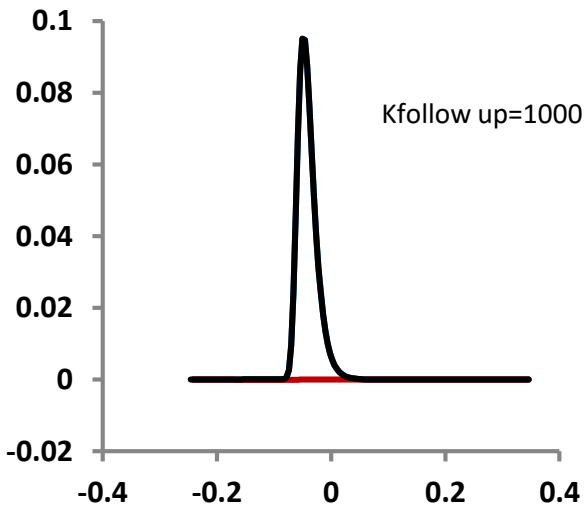
0.6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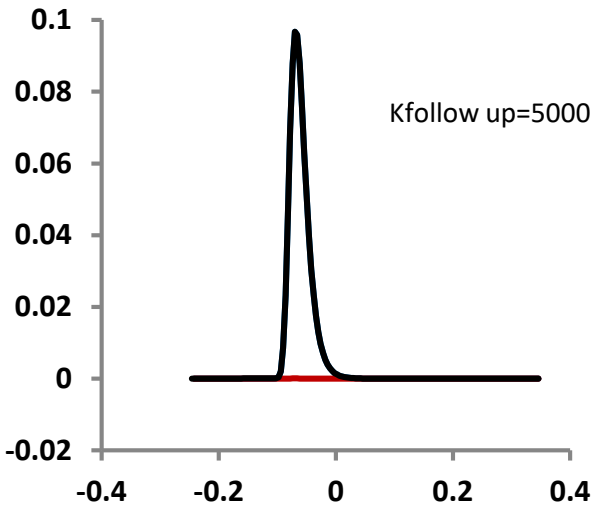
0.4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-0.02
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0.2
0.4
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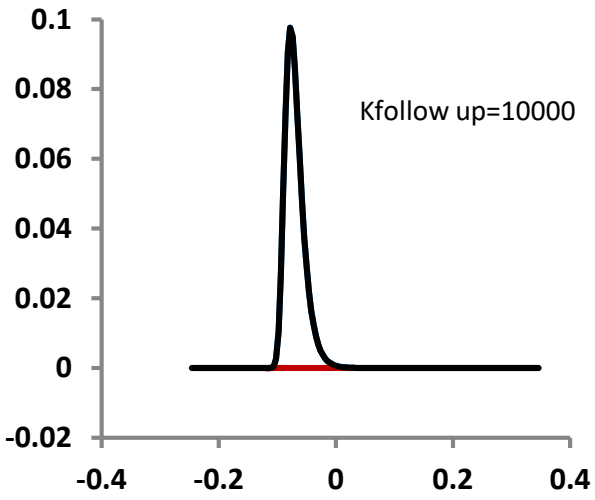
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0.2
0.4
Kfollow up=10000

$Ks=10^{0}$

U=0.01

b=0.001

0.01

0.1

1

50

1000

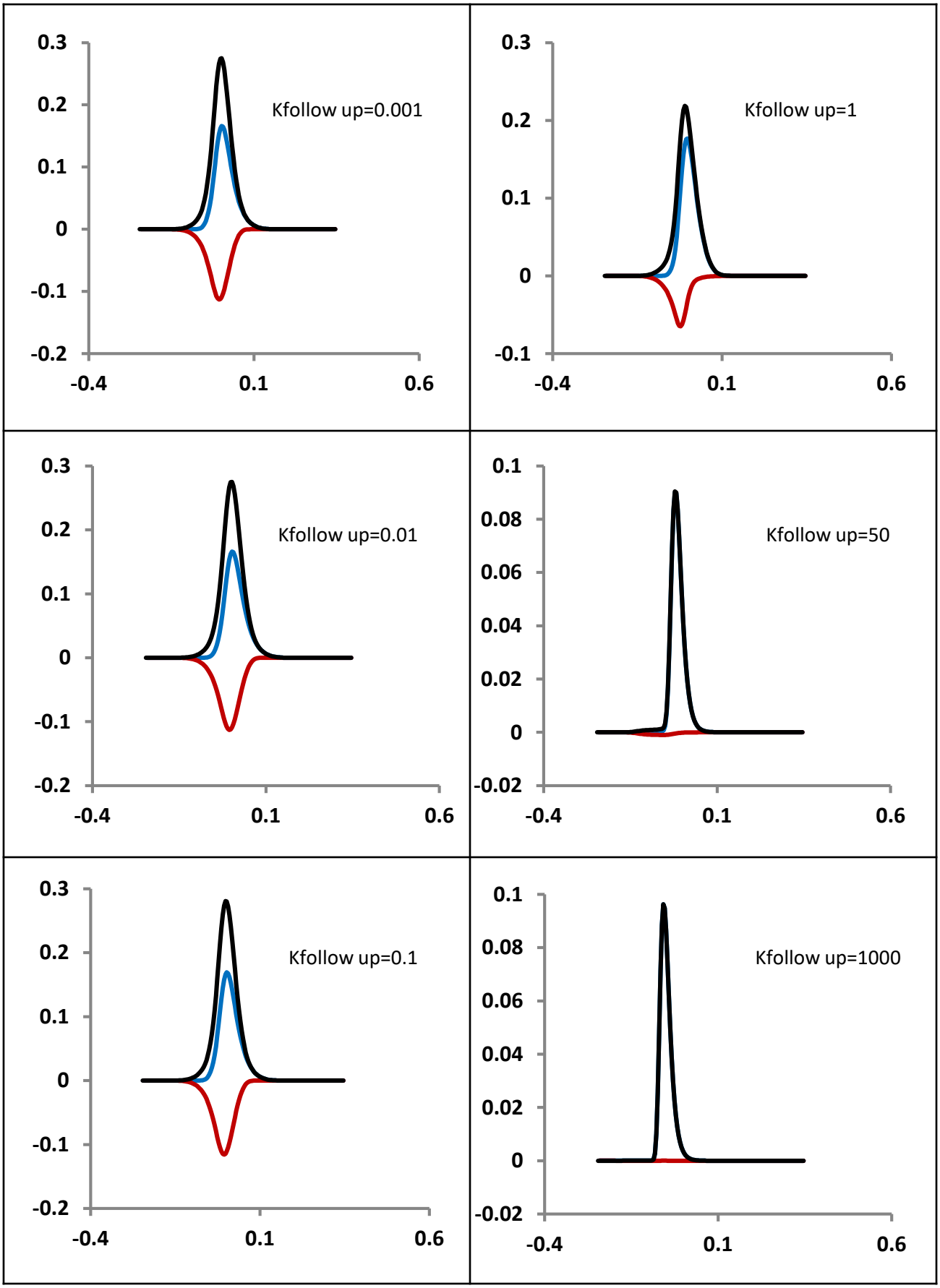
5000

10000

100000

1000000

- Epsilon 10^{minus3}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-0.2
0.08
0.06
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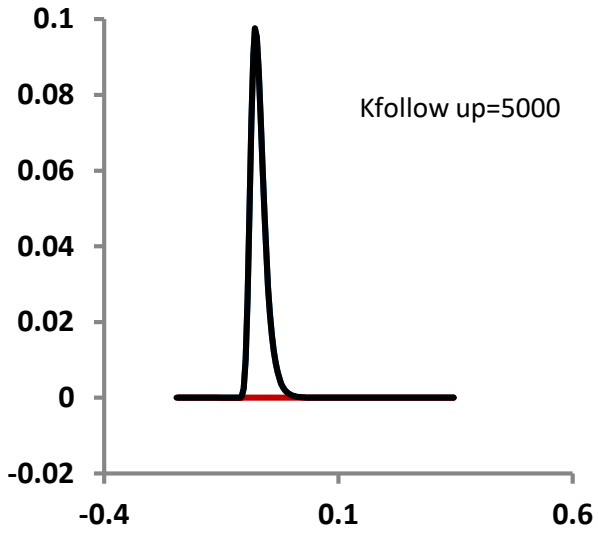
0.02
-0.02
-0.4
0.6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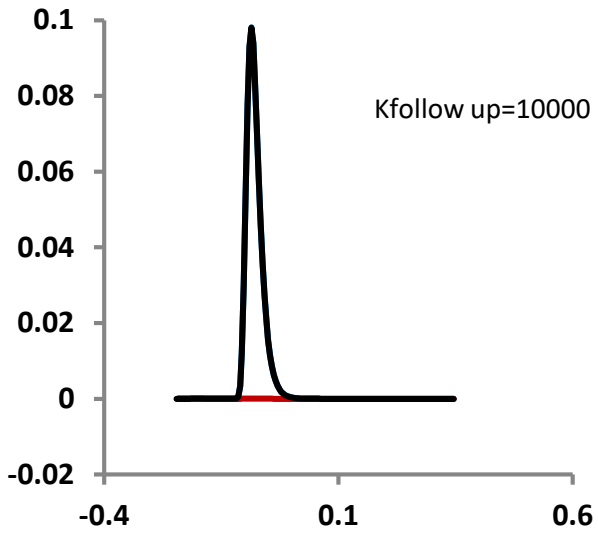
0.1
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-0.4
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Kfollow up=10000

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